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Density, Viscosity, and Electrical Conductance of Sodium and Potassium Hydroxide in Concentrated Aqueous Solution

Warren Lee Erdahl

DENSITY, VISCOSITY, AND ELECTRICAL CONDUCTANCE OF SODIUM AND POTASSIUM HYDROXIDE IN CONCENTRATED AQUEOUS SOLUTION

BY

WARREN LEE ERDAHL

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This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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Thesis Advisor Date

Head, Chemistry Department Date

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INTRODUCTION

There has been much work done in the area of measurement of properties of dilute solutions. As a result various relationships describing these properties have been observed. The region over which these relationships apply is narrow and limited to solutions of very low concentration. Some attempts have been made to extend these relationships to regions of greater concentration, but only limited success has been achieved. Most attempts are limited by insufficient knowledge of the properties of the concentrated solutions.

The purpose of this research is to look at various properties of concentrated aqueous sodium and potassium hydroxide solutions and their mixtures. Because of research activity in the areas of alkaline batteries and fuel cells, more knowledge of the physical and chemical characteristics of these solutions at various temperatures is needed.

Some work has been done in the area of equivalent conductance of these solutions. But to extend the relationships to higher concentration, knowledge of the viscosity of these solutions is needed.

Accurate viscosities of these solutions have been measured by determining the resistance of flow of these solutions in a small diameter tube (Ostwald viscometer). Differences in the two solute solutions were noticed, and the similarities and changes of the mixture solutions to the pure solute solutions were observed.

From this investigation various relationships were tried and new relationships proposed. The Root equation for the concentration dependence of density was tried, and a new expression was proposed

for concentrations expressed in mole fractions. Several concentration dependent equations for viscosity were tried, and most failed. As a result modifications of existing theories were tried, and various degrees of success were achieved for both the viscosity of pure electrolytic solutions and solutions of mixed electrolytes. The existing temperature dependent equations for density proved to be adequate. A zero mobility theory for the temperature dependence of viscosity and electrical conductance was tried, and some of the consequences of this theory were investigated.

HISTORICAL

Basic Concepts

The purpose of this section is to review the terminology, basic methods of determination of the quantities being looked at, and other important concepts relative to density, viscosity, and conductance studies.

For a more complete discussion on the basic concepts of density, there are references, such as, Techniques of Organic Chemistry, edited by A. Weissberger (1). Density is defined as the mass of a substance divided by its volume. In the cgs system of measurement, its units are grams per cubic centimeter.

Absolute density, d^t, is the density of a substance measured at a specific temperature, t°C. The density expressed in grams per milliliter is more commonly used, but because the difference in cubic centimeters and milliliter is small, the two are often used interchangeably ($1\ cm^3 = 1.000027$ ml).

Relative density, d_4^t, gives the ratio of the absolute density of a substance at t°C to that of the absolute density of water at its temperature of maximum density, 3.98°C. This is commonly referred to as the "specific gravity relative to water at 4°C."

Specific gravity, d_t^t, is the ratio of the mass of a substance at t°C to the mass of an equal volume of water at the same temperature. Both relative density and specific gravity are dimensionless numbers.

The density of a liquid is determined by measuring the mass of a specific volume of the liquid. The actual manner by which this is done is a matter of choice. There are numerous ways of measuring both quantities.

Detailed discussions on viscosity and its measurement can be found in the literature (2,3,4,5). The coefficient of viscosity, η, is given by the following expression:

$$f_x = (\partial v_x/\partial z)\eta$$

where f_x = the shearing force per unit area of fluid

$(\partial v_x/\partial z)$ = the velocity gradient

The unit of viscosity is the poise, defined as the viscosity of a material which requires a shearing force of one dyne per square centimeter to maintain a velocity gradient of one centimeter per second between two plates one centimeter apart. The units of the poise are g/cm-sec. The centipoise, 1/100 of a poise, is commonly used.

Fluidity, ϕ, is the reciprocal of the absolute viscosity. Fluidity is expressed in units called rhe, $(\text{poise})^{-1}$.

Kinematic viscosity, ν, is equal to the absolute viscosity divided by the absolute density of the liquid. This is the easiest type of viscosity to measure, because no previous knowledge of the liquid density is required. The unit of kinematic viscosity is the stoke, with the units of cm^2/sec.

Relative viscosity, η_{rel}, is the ratio of the absolute viscosity, η, divided by the absolute viscosity of a reference liquid, η_o. The specific viscosity, η_{sp}, is similar. It is the ratio of the difference between the solution's viscosity and the solvent's viscosity divided by the solvent's viscosity.

The measurement of the flow of a liquid through a long capillary tube of circular cross section is the most common method used for determining the viscosity of a liquid of relatively low viscosity. Three general assumptions (3) are made to simplify the solution of the viscosity equation for use with a capillary tube.

1. The liquid is assumed to be a Newtonian, incompressible liquid.
2. It is assumed that the flow is laminar, with flow lines parallel to the cylinder walls.
3. The layer next to the wall is assumed to stick to the wall, so its velocity is zero.

The equation for the laminar flow of a Newtonian liquid through a cylindrical capillary tube is most commonly given as (2,4):

$$\eta = \frac{\pi r^4 dght}{8V\ (1+nr)} - \frac{mdV}{8\pi(1+nr)t}$$

Most of these terms are dimensions of the viscometer and are very difficult to evaluate accurately. They can be determined indirectly by placing the equation in this form:

$$\frac{\eta}{d} = At - \frac{B}{t}$$

where

$$A = \frac{\pi r^4 gh}{8V(1+nr)} \qquad \text{and} \qquad B = \frac{mV}{8\pi(1+nr)}$$

A and B are then determined by measuring the efflux times and densities of two reference liquids of accurately known viscosity. Two equations with two unknowns are obtained, and the simultaneous solution of these will give the values of A and B. Once A and B are known, the viscosity of any other liquid can be determined by measuring its efflux time in the same viscometer and its density.

An explanation of the terms used in conductance studies and discussions of the basic concepts involved are covered more thoroughly in many texts (3,6,7), but a brief summary is presented here.

The flow of current through a conducting medium is best described by Ohm's law:

$$E = IR$$

where E = electromotive force (volts)

I = current (amperes)

R = resistance (ohms).

The resistance is a function of the intrinsic properties of the conducting medium and its geometry:

$$R = \frac{\rho l}{A}$$

where l = length of the conducting medium

A = cross sectional area of the conducting medium

ρ = the intrinsic properties of the conducting medium.

The term, p, is the specific resistance of the material or the resistivity, and it has the units, ohm-cm. The reciprocal of the specific resistance is termed the specific conductance or conductivity, K, and has the units, $ohm^{-1}\text{-}cm^{-1}$.

The reciprocal of the resistance, R, is termed the conductance, L, and has the units, $ohms^{-1}$.

The conductivity of an electrolytic solution is dependent on the nature of the ions present and their concentration. When referring to a specific electrolyte in a particular solvent at a specified temperature and pressure, the equivalent conductance is the term used to describe the conductance behavior.

$$\Lambda = 1000K / c$$

where Λ = equivalent conductance

K = conductivity

c = concentration (normality)

The resistance of a solution is measured by passing an alternating electric current through a Wheatstone bridge circuit and balancing the resistance of the solution against known resistances. The cell containing the solution acts similar to a capacitor in parallel with a resistor. To reduce this effect a variable capacitor is placed in parallel with the known resistances. For very precise work further modifications are necessary.

Determining the dimensions of the cell is very difficult, therefore, the cell is calibrated by measuring the resistance of a solution of accurately known conductivity. Once the cell constant is known,

the resistance of any other solution can be measured and the conductivity calculated.

In studies made by A. Woo (8) the conductivities of solutions of NaOH, KOH, and their mixtures were determined. When the conductivity was plotted against the concentration of the solutions, a maximum in the curve was observed. References to other cases of similar behavior were made. Changes in conductivity may in part be due to a change in the number of ions conducting the current or to the mobility of the ions.

The Bjerrium theory (9) would explain the maximum in the conductivity curve on the basis of a decrease in the number of ions conducting the current. He has postulated that associated ion pairs can be formed. These ion pairs can be represented as:

$$C^+ + A^- \rightleftharpoons (C^+A^-) \rightleftharpoons CA$$

$$(C^+A^-) + C^+ \rightleftharpoons (C^+A^-C^+)^+$$

$$(C^+A^-) + A^- \rightleftharpoons (A^-C^+A^-)^-$$

For solutions of weak electrolytes the Bjerrium theory can not be expected to hold (9). There is also reason to wonder if a solvent with a high dielectric constant, such as water, will permit the ion pairs to form (10).

There have been many relationships formulated to describe the concentration dependence of the equivalent conductance. Most of these relationships are for very dilute solutions. A. Woo (8) has reviewed many of these relationships, and has attempted to extend a few to the region of concentrated solutions. Little work has previously been

done in the area of a viscosity correction to the equivalent conductance equation. The Wishaw-Stokes equation (11) has been one modification that has had a fair degree of success (8,11,12,13). Primarily what has been done is to multiply the calculated equivalent conductance by the relative viscosity, as an empirical way of accounting for the viscosity effect on the mobility of the ions.

Previous Measurements and Studies

The densities of some concentrated solutions of NaOH and KOH have been measured and studied (14,15,16). There are reported differences between the work done by G. Akerlof (15) and the International Critical Tables (14). G. Akerlof in his papers published only calculated tables relating to his results; the actual densities that were measured were never published. In observing changes in density over a particular temperature range, certain abnormalities appeared in Akerlof's work as the concentration increased that were not present in the International Critical Tables. For these two reasons the density values given in the International Critical Tables were believed to be more reliable. Akerlof stated in his article that the differences between the two sets of data partially balance each other out and actually they do not on the whole give any large discrepancies in density, although individual points may be found where differences appear even in the third decimal place.

The viscosities of some NaOH and KOH solutions have also been determined (17,18,19). There were large differences in the reported

values among the papers, and some noticeable errors in one paper in particular (18). For the work being investigated here, more comprehensive data were needed, therefore, these papers were used as a check on the accuracy and reliability of the method of investigation used in the present work.

The conductivity of concentrated solutions of NaOH, KOH, and their mixtures has been intensively studied by A. Woo (8); therefore, it was felt that no further determinations in this area were necessary at the present time.

Many different attempts have been made to find a concentration and a temperature dependence equation for density, viscosity, and conductivity. Some of these attempts have been based on theory, while others have been purely empirical. A review of the more common and successful equations will be presented here.

The relationship between the density of a solution and the concentration of the ordinary electrolyte in water has often been expressed by the Root equation (1,20,21):

$$d - d_o = Ac + Bc^{3/2}$$

where d = density of the solution

d_o = density of the solvent

c = concentration of the electrolyte (normality)

A and B = empirical constants.

W. C. Root (21) states that for solutions of alkali and alkaline earth halides, this equation holds to concentrations as high as 10 N, and for sulfuric acid solutions to a concentration of about 25 N.

All values calculated were claimed to be within experimental error.

G. J. Janz et al. (22) in their studies on $NaNO_3$, $NaClO_4$, and NaCNS solutions have used a similar type equation to express the concentration dependence equation for the densities of their solutions. For a concentration range of 0.1 M to 11 M they used the following expression:

$$d = A + Bc + Cc^2$$

A,B, and C are empirical constants obtained by a least squares fit to the data. A standard deviation of no more than 0.0007 g/ml was obtained.

The temperature dependence of the density is often talked about, but few people have ever put the relationship in terms of an equation (23,24,25,26,27). One of the more common forms used is:

$$d_t = d_{t_o} - B(t - t_o)$$

where d_t = density of the solution at temperature, t^oC

d_{t_o} = density of the solution at some temperature, $t_o{}^oC$

B = change in density per degree between t and t_o.

This relationship assumes that the temperature dependence is linear, but for a wide temperature range this does not hold. If a small range is used, quite satisfactory results can be obtained.

Another form commonly used is of the type

$$d_t = A - Bt$$

where t = temperature

A and B = empirical constants.

A. N. Campbell and D. F. Williams (24) have gone to an exponential equation

$$d_t = A\exp(BT)$$

where T = temperature in degrees Kelvin

A and B = empirical constants.

The temperature dependent equations presented were used in solution studies and molten salt studies.

For dilute solutions of electrolytes the Dole-Jones equation has been the relationship most commonly used to describe the concentration dependence of the solution's viscosity (20,28,29,30,31,32). The Dole-Jones equation is usually presented in the form

$$\frac{(\eta/\eta_o) - 1}{\sqrt{c}} = A + B\sqrt{c}$$

where η = viscosity of the solution

η_o = viscosity of the solvent

c = concentration of the electrolyte (molarity)

A and B = empirical constants.

A plot of $\frac{(\eta/\eta_o) - 1}{\sqrt{c}}$ versus $\sqrt{c}$ gives a straight line, the slope of which is B, and the intercept at $\sqrt{c} = 0$ is A. This equation does not hold above a concentration of 0.1 normal. Attempts have been made to extend this equation to regions of higher concentration (20,30,32). M. Kaminsky (32) found that by adding an extra term to the Dole-Jones equation, the relationship could be extended to a region of concentration above 0.1 N. His extension has become known as the Dole-Jones-

Kaminsky equation, and is used as

$$\eta/\eta_o = 1 + AM^{1/2} + BM + CM^2$$

where M = concentration (molarity)

A, B, and C = empirical constants.

P. Claessens et al. (30) used the ional concentration of the electrolyte, and were able to extend the range of the Dole-Jones-Kaminsky equation to an ional concentration of 17. The ional concentration of an electrolytic solution is

$$\Gamma = \sum M_i Z_i^2$$

where Γ = ional concentration

M_i = concentration in moles per liter of an ion, i.

Z_i = ionic charge on the individual ion, i.

Substituting the ional concentration into the Dole-Jones-Kaminsky equation, the relationship now becomes

$$\eta/\eta_o = 1 + A\Gamma^{1/2} + B\Gamma + E\Gamma^2$$

For the sulfuric acid solutions they were working with, an ional concentration of 17 is over 2 M.

H. Hagnas (20) took the Dole-Jones-Kaminsky equation and added two more terms. The terms added were not constant, but were modified to fit the equation to each set of data that were determined. In general form his equations can be represented as

$$\eta/\eta_o = 1 + Ac^{1/2} + Bc + Cc^{3/2} + Dc^2 + Ec^x$$

where c = concentration of the electrolyte (molarity)

x = an integer exponent on the last term that varies with the electrolyte being used. x is greater than 2.

A, B, C, D, and E = empirical constants

The results obtained for the salts of many metal perchlorates were very good, but the concentration of these solutions never exceeded 2 molar.

For the regions of high concentration, all the equations used have been empirical in nature. Some of these equations have had a fair degree of success. Some of the more successful equations are reviewed here.

L. L. Ezrokli (33) has found while working with concentrated $CaCl_2$ solutions that the log of the relative viscosity can be fitted into the following equation

$$\log \eta/\eta_o = Ac + Dc^3$$

where c = concentration (normality)

The $CaCl_2$ solutions considered were as high as 40% by weight.

S. P. Moulik (34) proposed a viscosity-concentration dependence equation which he describes as being applicable beyond the Einstein region. The Einstein equation for the concentration dependence of viscosity is

$$\eta/\eta_o = 1 + Kc$$

where c = concentration (molarity)

K = a constant for the solution.

The Einstein equation is generally considered to be applicable to very dilute solutions, approximately 10^{-3} molar or less. To the differential equation of the Einstein equation, Moulik had noted that concentrated solutions of electrolytes and nonelectrolytes seemed to follow the following trend:

$$\frac{d(\eta/\eta_o)}{d(c)} \quad \frac{(\eta/\eta_o)}{(c)} = K'$$

Integrating over small changes of c and η/η_o, this expression gives

$$(\eta/\eta_o)^2 = M + K'c^2$$

When a plot of $(\eta/\eta_o)^2$ versus c^2 is made, the resulting curve is straight except at the low concentration end. The straight part of this curve is then considered the region beyond the Einstein equation. This equation has had some degree of success with concentrated solutions of HCl, NH_4OH, NaCl, and urea, but others such as $LiClO_3$, and NaBr have not been as successful.

G. J. Janz and his coworkers (22,35) have formulated several empirical equations to show the viscosity-concentration dependence of concentrated solutions of NaCNS, $NaClO_4$, and $NaNO_3$. In earlier work on NaCNS solutions, the following equation was used to fit the viscosity data between 2 M and 11 M:

$$\eta = A + Bc + Cc^2 + Dc^3$$

where c = concentration (molarity).

In later work the equations were broken up into two regions, the region below 4 M, and the region above 4 M. The equations used were as varied as the electrolytes and the concentration regions.

The standard deviation in the region below 4 M for the relative viscosity was no larger than $\pm$ 0.004, and in the region above 4 M the standard deviation was no more than $\pm$ 0.03.

In some recent work on molten salts and concentrated solutions, C. A. Angell (36) and G. J. Janz et al. (22) have looked at a new type of equation:

$$1/\eta = A\exp\left[-k/(N_o - N)\right]$$

where A and k = empirical constants

N = concentration (normality)

N_o = the concentration of a solution at a specified temperature at which the solution becomes a glass.

Not much work has been done in this area, so it is difficult to evaluate its significance at this time.

The temperature dependence of the viscosity of a solution has been given by the Arrhenius equation (37)

$$\eta = A\exp\left[E_{vis}/RT\right]$$

where E_{vis} = activation energy for viscous flow

R = gas law constant

T = temperature in degrees Kelvin

A = an empirical constant.

This has been used more in the area of very dilute solutions and molten salts. For more critical work in concentrated solutions, other empirical relationships have been used such as

$$\eta = A + BT + CT^2 + DT^3$$

More recently the Fulcher equation has been reinvestigated (26, 38). The Fulcher equation is similar to the Arrhenius equation, except that an extra term, T_o, is added. The temperature dependence equation now becomes

$$\eta = A\exp\left[B/(T - T_o)\right]$$

where A and B = empirical constants

T = temperature in degrees Kelvin

T_o = the temperature at which the solution becomes a glass.

T_o is called the zero mobility temperature, and can more completely be defined as the temperature at which all rotational movement of the molecules or ions ceases, and only vibrational motion remains.

Some workers used a modified Fulcher equation (36,39) in their studies to achieve a better fit to the existing data. The modified equation used, is of the form:

$$\eta = AT^{1/2}\exp[B/(T - T_o)]$$

There are other features about the concentration dependence and temperature dependence equations involving N_o and T_o, but they will be discussed more thoroughly in a later section.

There has been one attempt to combine a concentration dependence equation with a temperature dependence equation (40). This equation is only an approximation, because only a simple exponential function for the concentration was used, and the Arrhenius temperature dependent equation was used. The equation is general and can be used with any electrolyte. The combined equation is given as

$$\eta / \eta_o = AT^{1/2} \exp(BP_m c/T)$$

where A and B = empirical constants

T = temperature in degrees Kelvin

c = concentration (molarity)

P_m = molecular weight of the solute including the water of hydration.

Values for A and B were given (A = 0.0565, B = 0.0902). For the electrolytes used in this study an accuracy of 4.5% was obtained.

Much of the work done in the area of the concentration dependence of conductance has been reviewed by A. Woo (8). One of the more recent treatments (22,39,41) has been

$$\Lambda = A \exp -k/(N_o - N)$$

where Λ = equivalent conductance

N = concentration (normality)

N_o = zero mobility concentration

A and k = empirical constants.

The temperature dependence of the conductivity is generally expressed as a linear function in temperature (24,25) for narrow temperature ranges:

$$K = A + BT$$

For a broader temperature range more terms are introduced such as

$$K = A + BT + CT^2$$

Conductivity as well as equivalent conductance have also been expressed in an Arrhenius type equation (24,25,42):

$$K = A \exp(-E_K /RT)$$

and

$$\Lambda = A\exp\ (-E_{\Lambda}\ /RT)$$

where T = temperature in degrees Kelvin.

Most of this work has been done in the area of molten salts. H. Bloom has pointed out that a more complete equation would be

$$\Lambda = A_1\ \exp(-E_1/RT) + A_2\exp(-E_2/RT)$$

where the subscripts, 1 and 2, refer to the cation and anion respectfully. This equation applies over a considerable range of temperatures for a variety of molten salts.

A modification to the Arrhenius equation (36,39,41) has been successful in showing the temperature dependence of the conductance of both concentrated solutions and molten salts:

$$\Lambda = AT^{-1/2}\ \exp\ [-k/(T - T_o)]$$

where A and k = empirical constants

T = temperature in degrees Kelvin

T_o = zero mobility temperature.

The concept of zero mobility temperature and zero mobility concentration has been applied to both the areas of conductance and viscosity in an attempt to show the similarity between the two transport properties. Walden's rule was the first attempt to show this similarity. It stated that the viscosity-equivalent conductance product was a constant. Studies in concentrated solutions have shown that this is not completely true. Advocates of the zero mobility temperature and concentration theory believe that if the same T_o and

N_o values can be obtained from both conductance and viscosity processes, this shows that the transport mechanisms are the same. C. A. Moynihan (39) has shown that the T_o and N_o values for molten $Ca(NO_3)_2 \cdot 4H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$ are within experimental error. For the $Ca(NO_3)_2 \cdot 4H_2O$ a value of 201°K was obtained for the conductance study and 205°K for the viscosity study. For the $Na_2S_2O_3 \cdot 5H_2O$, values of 203 and 204°K were obtained. G. J. Janz et al. (22) in their studies with concentrated solutions of $NaNO_3$, Na_2ClO_4, and NaCSN have not had similar results. The N_o values for these solutions are considerably different for the equivalent conductance and fluidity transport mechanisms. The N_o values obtained were: for $NaNO_3$ $N_o^{\Lambda} = 46$ and $N_o^{\phi} = 29$, for $NaClO_4$ $N_o^{\Lambda} = 32$ and $N_o^{\phi} = 19$, and for NaCSN $N_o^{\Lambda} = 23$ and $N_o^{\phi} = 20$. This would seem to indicate that the transport mechanisms are different for the two processes.

Recently, work on diffusion of ions has shown that it too can be fitted to the same general temperature dependent equation. Thus the general equation which approximately fits all three transport processes can be given as (43):

$$D/T, \Lambda, 1/\eta = AT^{-1/2} \exp\left[-k/(T - T_o)\right].$$

It would be nice if all solutions and molten salts followed these simple relationships, but the systems are far more complex than these relationships show. It is felt that a basic understanding might be gained by further research in this area. For instance it has been shown that the temperature dependent equation does not hold near the T_o temperature, but it holds quite well above the critical T_o temperature (26).

EXPERIMENTAL

Description of Equipment

In order to keep the solutions being tested at the same temperature throughout the duration of the determination, a constant temperature bath was used. Because of the caustic nature of many of the solutions being tested, and because of the need of a glassed walled container to hold the viscometers, two modifications were made to the normal constant temperature bath setup.

To keep the caustic solutions out of the bath water during the density determination, a tin lined container was set into the bath so the water could circulate around it. The pycnometers were set around the inside edge of this container and were held tightly in position by a wire screen that kept them pressed to the wall. A stirrer was placed in the middle of the container to keep the water evenly stirred at all times, so a temperature equilibrium could be maintained between the water in the bath circulating around the container and the water in the container. A thermometer was placed inside the container to measure the actual temperature that the solutions were being held at. It was possible to maintain the temperature inside the container to within $\pm 0.05^{\circ}C$ of the temperature specified.

The upper fiducial bulb of the viscometer had to be submerged during the entire time of the viscosity determination. This necessitated having a clear walled container in order to observe the upper and lower fiducial marks. Since the Lauda constant temperature bath

had insulated metal walls, a glass walled container was placed in the bath so the top of it was 3-4 inches above the level of the water in the bath. Water was pumped into the glass container from the bath's pumps and was allowed to overflow, while the water in the bath was circulating around it. In this manner the temperature was kept uniform throughout the depth of the glass container. A thermometer was placed inside the container holding the viscometers in order to measure the temperature at which the viscometers were being held. In the 20 to 45°C range it was possible to maintain the temperature inside the container to within ±0.05°C of the temperature specified. In the 55 to 75°C range the temperature was only able to be maintained to within ±0.10°C of the specified temperature.

The thermometers used were narrow ranged thermometers. The one used in the 0 to 50°C range was subdivided into 0.1°C intervals. The other thermometer was broader ranged. Its range was from 0 to 110°C in 0.2°C subdivisions. The two thermometers were calibrated against each other in order to keep the temperature intervals the same.

An electric timer and a stop watch were used to determine the efflux times of the solutions in the viscometers. A five minute timing of the two instruments against each other gave only a 0.1 sec difference between the two. Part of this error could have been operator error. The electric timer was calibrated in 0.1 sec intervals, while the stop watch was calibrated in 0.2 sec intervals.

The pycnometers used were of the Guy-Lussac or Weld type. They were approximately 25 milliliters in volume. The capillary tube was

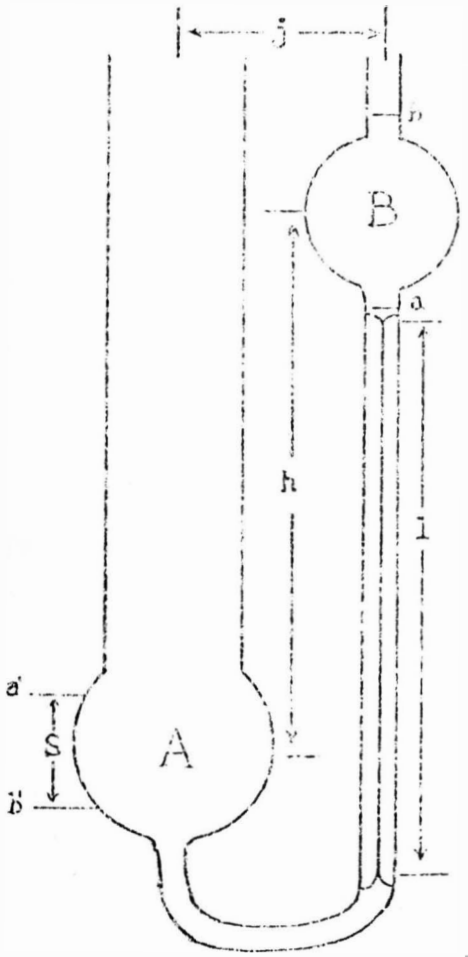
fitted by a ground glass joint to the main body of the pycnometer. There were no expansion cups or caps provided with these pycnometers.

The viscometer used was of the Ostwald type. Figure 1 gives a sketch of an Ostwald viscometer with its important features labeled. Two viscometers were used in this work. Their dimensions and important features are listed in Figure 1.

Preparation and Analysis of Solutions

The preparation of pure water (1,45,44) is very important, because it was used to calibrate both the pycnometers and the viscometers. It was also used in the preparation of all standard and test solutions. Because even the smallest impurity in the capillary tube of the viscometer could alter its calibration, the viscometers were rinsed thoroughly several times with purified water to be sure all contaminates were removed.

Singly distilled water was redistilled in an all pyrex system after a slight amount of KOH and $KMnO_4$ was added to the distillation flask to aid in the oxidation of organic contaminates. The water was then stored in an acid cleaned pyrex flask fitted with an ascarite trap to prevent the absorption of carbon dioxide gas from the air. Before the water was used for making solutions or calibrating the instruments, it was boiled to drive off all dissolved air in the water. A conductivity measurement was made to check the purity of the water. A qualitative measurement of 5×10^{-6} ohm^{-1} was obtained.



A = lower fiducial bulb
B = upper fiducial bulb
a = lower fiducial mark
b = upper fiducial mark
l = length of the capillary tube
r = radius of the capillary tube
h = difference in the levels of the two free liquid surfaces when half the efflux time has elapsed
j = horizontal distance between the upper and lower bulbs of a U-tubed viscometer
V = volume of liquid flowing from or into the upper fiducial bulb
$\dot{V}$ = volume of charge placed into the viscometer
a' = level of meniscus when liquid is drawn up to mark a
b' = level of meniscus when liquid is drawn up to mark b
S = distance between a' and b'
V_A = volume of bulb A
r_A = radius of bulb A
r_B = radius of bulb B

dimension	viscometer 1	viscometer 2
l	10.0 cm	10.0 cm
r	0.03 cm	0.025 cm
V	3.10 cm^3	2.05 cm^3
$\dot{V}$	5.00 cm^3	7.00 cm^3
j	1.6 cm	1.8 cm
h	13.3 cm	12.2 cm
S	1.5 cm	0.5 cm
V_A	5.3 cm	10.5 cm
r_A	0.90 cm	1.10 cm
r_B	0.80 cm	0.65 cm

Figure 1. Diagram of an Ostwald Viscometer

This indicated that the water very closely approximated conductivity water.

The preparation of NaOH solutions can be found in many places (15,45). An initial solution was made by dissolving approximately 4 kilograms of analytical grade NaOH in 7 liters of purified water in an acid cleaned pyrex flask fitted with an ascarite trap to prevent the absorption of carbon dioxide. The solution was allowed to sit a few days to allow any carbonate precipitate to settle out. The solution was then decanted off, and the individual solutions were mixed using the stock solution and purified water. All of the individual solutions were stored in acid cleaned pyrex flasks fitted with ascarite traps.

The concentration of the following solutions was determined in the indicated manner. An approximately one molar solution was made from the stock solution, and was standardized with dried primary standard potassium acid phthalate to a phenolphthalein end point. Several determinations of the base's concentration were made in order to get as accurate a determination as possible. The standard deviation was 0.0006 gram-equivalents per liter. Then a two molar solution of hydrochloric acid was standardized against the base by pipetting 50 ml of the standardized base into a flask and titrating it with the acid to a phenolphthalein endpoint. The 50 ml pipet was previously calibrated to be 50.000 ml $\pm$ 0.002 ml. The standard deviation in the acid determination was 0.0005 gram-equivalents per liter. The individual solutions being investigated were standardized against the

standard hydrochloric acid. An amount suitable for titration with the hydrochloric acid was weighed out accurately on an analytical balance and titrated to a phenolphthalein end point. The densities of the solutions were determined at 25.0°C and their volume calculated. The normalities of the solutions were then calculated from the preceding information. Several determinations were made on each solution to achieve as accurate a determination as possible. An average deviation of 0.003 gram-equivalents per liter was obtained on most solutions.

Discussion of the preparation of KOH solutions can also be found in several places (16). A stock solution was made by dissolving 4 kilograms of analytical reagent KOH in 4.5 liters of purified water in an acid cleaned pyrex flask fitted with an ascarite trap to prevent absorption of carbon dioxide. The solution was allowed to sit for a few days to allow any carbonate precipitate to settle out. Individual solutions were made by diluting the decanted stock solution with carbonate free purified water. The solutions were then stored in acid cleaned pyrex flasks fitted with ascarite traps. The concentrations of these solutions were determined in the same way as the NaOH solutions were determined.

The mixtures of NaOH and KOH were made by pipetting an exact amount of NaOH solution into a pyrex flask with a calibrated 50 ml pipet and then adding the appropriate number of equivalents of KOH solution by use of a 50 ml buret. The concentrations of the mixtures were calculated from the normalities and volumes of the NaOH and KOH solutions used by assuming the volumes were additive.

The preparation of sucrose solutions for viscosity work is described in a monograph published by the National Bureau of Standards (46). The sucrose solutions used were made by weighing sucrose that had been dried three days in a $CaCl_2$ desiccator, adding purified water and then weighing the total mass. The percent sucrose by weight was then calculated.

The sucrose solutions were analyzed by the use of a sodium light and a polariscope. For a 20.04% sucrose solution by weight, the polariscope gave determinations of 20.09% and 19.89% sucrose by weight. All sucrose solutions made were considered to be more accurately standardized by using the actual weights of the sucrose and water weighed out. Solutions of 20.0%, 30.0%, 40.0% and 45.0% sucrose by weight were made and used as standards for determining the viscometer constants.

Procedure

A detailed procedure for accurate density determination can be found in Technique of Organic Chemistry, edited by A. Weissberger (1). Various methods, techniques, and instruments are discussed therein.

The Guy-Lussac or "Weld specific gravity bottle," a pycnometer without expansion cup or a cap, is a convenient, versatile instrument for determining the density of a fluid, if an accuracy of only 1×10^{-4} grams per cubic centimeter is needed. The accuracy is limited, because the volume of the pycnometer can vary due to the variance of

pressure that can be exerted on the ground glass joint of the capillary tube.

Certain precautions in handling and weighing the pycnometer must be observed. For greater accuracy the pycnometer should never be heated excessively above or cooled below the temperature at which it was standardized. This causes the pycnometer's volume to change, and once the stress is released, the change back to the original volume is very slow. A newly made pycnometer is apt to undergo volume changes for a period of weeks. Because of the inherent inaccuracy of volume in the Weld pycnometer due to the variance in pressure on the ground glass joint, the effects of this change in temperature on the volume of the pycnometer were not observed.

The pycnometers needed to be cleaned in potassium dichromate-concentrated sulfuric acid cleaning solution both before calibration and after use. This was accomplished by letting them soak in the cleaning solution over night, rinsing them thoroughly with distilled water in the morning, and then letting them soak in distilled water for a few hours before finally rinsing them and drying them in an oven at 110°C for one hour.

Because the weight of the pycnometer could increase by several milligrams by the adsorption of water from the air on its surface, the pycnometers were wiped with a clean lintless towel, and allowed to stand by the balance for a few minutes before weighing. Several weighings were made of each pycnometer after these wipings to get an average dry weight. Seldom did the dry weight vary more than a 0.4

milligram spread over the weighings. The filled bulbs were treated in a similar fashion to keep the weight of the bulb as nearly the same as possible. If the dry weights are erratic in behavior, this is possibly due to a build up of electrostatic charge on the pycnometer. This can be reduced by placing a safe amount of radioactive material in the balance to neutralize the charge.

In calibrating the pycnometers with pure water, the pycnometers were filled with a pipet and placed in a stirred constant temperature bath for thirty minutes or more to allow them to come to temperature. The excess fluid was forced out of the capillary by placing the ground glass joint back into the bulb in as nearly the same position each time as possible. Care had to be taken to try to apply the same amount of pressure to the ground glass joint each time. Each pycnometer was checked to see that there were no air bubbles in the pycnometer itself or under the ground glass joint. After a few minutes the tops of the capillary tubes were wiped clean, and the pycnometers removed from the constant temperature bath. The whole pycnometer was then dried with a lintless towel. It was necessary to keep the pycnometers in a cooler place than the temperature bath was, in order to keep fluid from being forced out of the capillary tube and evaporating at a faster rate than it normally would have. To lessen the error due to evaporation, it was necessary to try to keep the same interval of time between the removal of the pycnometers from the bath and the weighing of them.

Five or six different determinations of the weight of the standardizing liquid were taken to obtain a better average weight of the liquid in the pycnometer. If the weight of the liquid in the pycnometer varied more than ± 2 milligrams, the pycnometer was never used in a density determination.

The volume of the pycnometer was determined by dividing the density of the pure water into the weight of the water in each pycnometer. The values of the density of pure water at the various temperatures of standardization were taken from the 49^{th} edition of the CRC Handbook of Chemistry and Physics (47).

The same general procedure was used in running the solutions under investigation as in the standardization of the pycnometers. Three pycnometers were used to determine the density of the solutions under investigation. The average of these three determinations was taken to be the density of the solution. There was seldom more than a 0.2 milligram per milliliter difference spread between all three density values.

The densities of the NaOH solutions were determined at 25.0°C, 35.0°C, and 45.0°C. The densities of the KOH solutions and the solutions of the mixtures were determined at only 25.0°C. The International Critical Tables (14) gives the densities of many NaOH solutions whose concentration is expressed in weight percent at various temperatures. By assuming the density versus temperature curve as linear over a small temperature range, approximately 20°C, the change in density per degree can be calculated. The following equation was

then used to calculate the density of the solution at a different temperature

$$d_t = d_{t_o} - B(t - t_o)$$

where d_{t_o} = density of the solution at temperature, t_o

d_t = density of the solution at temperature, t

B = change in the density per degree of temperature.

Concentrations whose density values at 20°C were a little higher than the density values of the NaOH solutions being investigated at 25.0°C were chosen. The change in density between 40°C and 20°C was calculated and divided by 20 to get the change in density per degree, B. The density at t_o was chosen to be the measured density of the NaOH solutions at 25.0°C. The above formula was then used to calculate the densities of the solutions at 35.0°C. To check on the reliability of the method, the densities of the solutions were measured at 35.0°C and compared to the calculated values. An average deviation of less than 1×10^{-4} g per ml was obtained. As an extra check the same was done on the solutions at 45.0°C, and again the average deviation was less than 1×10^{-4} g per ml. Since the accuracy was almost as reliable as the actual measurement, the values of the densities at 55.0°C, 65.0°C and 75.0°C were calculated instead of being measured.

A detailed procedure for accurate viscosity determination can be found in publications by the American Society for Testing of Materials (44,48). These articles also include discussions of the degree of accuracy needed by other equipment used in the determination.

The viscometers were cleaned overnight in a warm potassium dichromate-concentrated sulfuric acid cleaning solution, and then rinsed thoroughly several times with doubly distilled water. The viscometers were then dried by rinsing them with reagent grade acetone and applying a vacuum to boil off any excess acetone remaining.

It was necessary to aline the viscometers with a plumb bob before an efflux time could be measured. After alinement the viscometers were securely mounted to insure their alinement throughout the duration of the run.

Doubly distilled and degassed water was used as a viscosity standard and for the preparation of the standard sucrose solutions used for determining the viscometer constants. The same pipet was used to deliver an exact amount of liquid into the viscometers each time. The pipets were periodically cleaned with cleaning solution to make sure their volume remained the same. The viscometers were then sealed to keep dust out and to reduce the amount of evaporation that might occur while the viscometers and liquids were coming to temperature in the constant temperature bath.

It was necessary to keep the upper fiducial bulb submerged all the time the viscometer was in the constant temperature bath in order to be certain that the fluid was kept at the specified temperature. The water in the bath was constantly stirred to keep an even temperature throughout the whole system. The viscometers were allowed at least thirty minutes to come to temperature before an efflux time was measured.

The liquid in the viscometer was adjusted by using gentle vacuum to draw it into the upper fiducial bulb. The efflux time was then measured. For best results the efflux time should be over three hundred seconds, but due to the large range of viscosities of the solutions being tested, this was not always possible. For water and the lowest concentrated solutions at higher temperatures, the efflux time was below one hundred seconds. To reduce possible error in the efflux time measurement, especially when the efflux times were short, several efflux time measurements were made on the same solution, and the average was taken to be the correct efflux time. If more than a 0.5% variance in the flow times occurred, the viscometer was recleaned in cleaning solution and the whole determination was repeated.

Two runs with two different viscometers were made on each solution, and the average of the four runs was taken to be the correct viscosity. If there was over a 1% difference in the spread of the values of the viscosity among the runs, the determination was repeated until better agreement was achieved.

The viscometer constants were determined at 20.0°C. The values for the viscosity of water were taken from the 43rd edition of the CRC Handbook of Chemistry and Physics (49). The values of the viscosity of the sucrose solutions used were taken from a monograph published by the National Bureau of Standards (50).

The viscosities of the NaOH solutions under investigation were determined at 25.0°C, 35.0°C, 45.0°C, 55.0°C, 65.0°C, and 75.0°C. For the KOH solutions and the solutions of the mixtures, the viscosities were determined at 25.0°C only.

Error Analysis

The purpose of this section is to examine the errors that affect density and viscosity determinations. The errors will be discussed, and where possible the magnitude of the error will be shown. There are several references (1,2,3,4,5,44,48) which cover these errors in greater depth, but a short review will be presented here.

Weight is defined as the mass of an object times the acceleration due to gravity acting on it. The weight of an object in one place is directly proportional to its weight in another place,

$$W_1/W_2 = mg_1/mg_2$$

If the weight is always determined at the same place, $g_1 = g_2$, therefore, $W_1 = W_2$. All weighings in this experiment were made in the same location, therefore, no corrections had to be made for the changes due to gravity.

The density of a liquid generally decreases with an increase in temperature. For pure, ordinary water at room temperature, the change is approximately 0.0003 g/ml $^{\circ}$C. For accurate density determination the temperature must be regulated to within at least $\pm$ 0.1°C to insure fourth place accuracy. The volume of the pycnometer increases with the change in temperature; this in part helps to compensate for the error if only small increases in temperatures are made. For the density determinations made in this work, a temperature control of $\pm$ 0.05°C was maintained. Little error was introduced by changes in temperature.

For a liquid with a boiling point well above the temperature at which its density is being determined, the effect of pressure on the solution is small. The density of water increases by only 0.00005 g/ml for every increase of one atmosphere of pressure. In a normal density determination the barometric pressure seldom varies more than 30 mm of Hg. Thus the effect of pressure on the system is negligible.

Impurities in a solution can have a relatively large effect on its density. A simple approximation as to the effect of an impurity is given by the following equation:

$$d = \frac{d_o d_1}{0.01 p_1 (d_o - d_1) + d_1}$$

where d = density of the mixture

d_o = density of the solvent

d_1 = density of the solute

p_1 = % weight of the impurity (g/100 g solution).

This equation is based on the assumption that the volume of the mixed solution is equal to the volume of the pure solvent plus the volume of the solute, that is, the volumes are additive.

In calibrating the pycnometers, water approximating conductivity water was used; therefore, the percent impurity was very small. There would be no observable change in the density of the water.

NaOH and KOH absorb water and carbon dioxide from the air, whether they are in the solid phase or solution. For this reason precautions were taken to prevent carbon dioxide from entering the systems. The

carbonates of these bases are insoluble in saturated solutions of the bases (51), but the stock solutions used in this study were not that concentrated. The stock solutions were analyzed to determine the carbonate content in them. Even after 20 months, a 5.00 ml sample of the NaOH stock solution, which was titrated with 2.28 N HCl, gave only a 0.05 ml difference between the phenolphthalein and methyl orange end points. The KOH stock solution needed 0.07 ml of the acid solution. A water blank needed 0.03 ml of the acid solution to reach the methyl orange end point that was used for the stock solutions. Really all that can be concluded is that the carbonate concentration is very low in these solutions. The molar concentration of the carbonates could be estimated to be on the order of 0.01 M Na_2CO_3 and 0.02 M K_2CO_3. Using the equation which approximates the increase in the density of a solvent due to impurities, there may be an increase of 5×10^{-4} g/ml in the density of the NaOH stock solution due to the Na_2CO_3 present and an increase of 8×10^{-4} g/ml in the KOH stock solution due to K_2CO_3. All the solutions used were made from dilutions of the stock solutions with carbon dioxide-free water. The carbonate concentration would be much lower in them; therefore, the increase in the density of the solutions would be much less.

The effect which dissolved air would have on the density of a liquid is small. At 20°C the difference in the density of air-saturated water and the density of air-free water is on the order of 4×10^{-7} g/ml. At higher temperatures this amount is even less. The water used for calibrating purposes was degassed, not because of the weight of air involved, but because dissolved air is released

in the form of bubbles which stick to the inside wall of the pycnometer displacing water which should be weighed. Water which was degassed did not produce these bubbles.

If an accuracy of no more than 0.1% is required, the following expression for the density of the liquid can be used:

$$d = (W'/W_o)d_o$$

where d = density of the liquid sample

d_o = density of the calibrating liquid

W' = uncorrected weight of the liquid sample

W_o = uncorrected weight of the calibrating liquid.

It is assumed in this expression that d/d_o is in the range 0.5 to 2.0, and the weights used in calibrating the pycnometer were the same weights used in weighing the sample. For more accurate work the bouyancy of the air must be accounted for. For an accuracy of 0.01% or fourth place accuracy, the following approximation can be used:

$$d = d' + c$$

where $c = D(1 - d'/d_o)$

D = density of the air.

This approximation is based on the assumption that the densities of the weights used and the air are constant for all weighings, including the calibration. For fourth place accuracy it is usually justified to assume $D = 0.0012$ g/ml. There are tables for values of c. For example, when $R = 1.2$ the value of c is -2.4×10^{-4} g/ml. This value is then added to the measured density value to obtain the corrected

density. For the most dense solution, the one in which R = 1.5, the correction was -6.0×10^{-4} g/ml.

These corrections were made on all density values determined in this work. But due to the inherent inaccuracy in the volume of the pycnometer due to the pressure that can be placed on the ground glass joint, no further corrections were made.

If one wanted to obtain a higher degree of accuracy, it would be necessary to correct all weighings to weight in a vacuum. To do this it would be necessary to obtain the balance room temperature, barometric pressure, and relative humidity every time a weighing was made. The following expression could then be used to calculate the density of the air in the balance room at the time of the weighing:

$$D = 0.001293(P - k)/(1 + 0.00367T)760$$

where $k = 0.0038HP^{t}_{H_2O}$

P = barometric pressure in the balance room

$P^{t}_{H_2O}$ = vapor pressure of water at $t^{o}C$ (can be obtained from standard tables)

H = relative humidity of the air in the balance room

T = temperature in degrees Centigrade in the balance room.

Summarizing the errors that could affect the density measurements, it can be seen that little error resulted from changes in acceleration due to gravity or changes in the barometric pressure. Even the amount of air dissolved in the sample had little effect on the weight, unless it formed bubbles on the inside walls of the pycnometer and displaced

liquid that should have been weighed. For this reason, water used in calibrating the pycnometer was degassed.

The temperature controls and bouyancy corrections used were within the limits to ensure fourth place accuracy. Due to errors in determining the volume and impurities, it was not necessary to take further precautions.

The largest error in measurement is that due to the measurement of the volume of the pycnometer. Because of its construction, there is an approximate error of 1×10^{-4} g/ml. The precision of the density values clearly showed this. For most determinations the average error was between 1×10^{-4} and 2×10^{-4} g/ml.

The carbonates in the stock solutions produced an uncertainty in knowing the density of the pure solutions by increasing the density of the solution over that of the pure solution. For the stock solutions this uncertainty may have been as high as 8×10^{-4} g/ml. For the least concentrated solutions this uncertainty decreased considerably.

The measurement of the flow of a liquid through a circular capillary tube is probably the most accurate method of determining viscosity used today (2). The most widely used viscometer (2) is one in which the pressure causing the flow arises from a hydrostatic head of liquid in the viscometer. The kinematic viscosity is obtained directly. Measurements are made by drawing the liquid up the capillary tube into the upper fiducial bulb and determining the time it takes for the liquid to flow back through the capillary tube into the

reservoir. If laminar flow of a Newtonian liquid can be assumed, the Poiseuille equation with corrections for the flow of the liquid at the ends of the capillary tube can be used to describe the viscosity of the liquid. The first term in the viscosity equation is the Poiseuille expression, and the second term is called the kinetic energy correction term:

$$\eta = \frac{\pi r^4 dght}{8V(l + nr)} - \frac{mdV}{8\pi(l + nr)t}$$

where η = viscosity of the liquid

r = radius of the capillary tube

d = density of the liquid sample

t = flow time of sample through the capillary tube (efflux time)

g = acceleration due to gravity

h = difference between the levels of the two free surfaces when the time is equal to $\frac{1}{2}t$

V = volume of the liquid flowing through the capillary tube

l = length of the capillary tube

m = coefficient of the kinetic energy correction (Hagenback correction)

n = coefficient of the Couette correction to the length of the capillary tube.

Although it is known that m and n are not constant over the entire range of Reynolds numbers, they remain sufficiently constant in some useful range to be treated as such (2). For the ideal case in which the Reynolds number is less than ten, n is equal to 1.146 and m is

equal to zero. If the Reynolds number is greater than ten, n is equal to 8.573 and m is equal to 1 (4).

The Reynolds number is defined as

$$R_e = \frac{vdj}{\eta}$$

where R_e = Reynolds number

v = average velocity of the liquid flowing through the capillary tube

j = horizontal distance between the upper and lower fiducial bulbs of a U-tube viscometer

d = density of the liquid sample

η = viscosity of the liquid sample.

The average velocity of the flowing liquid can be approximated by the following relationship:

$$v = \frac{V}{\pi r^2 t}$$

By definition if R_e is less than 2000, the flow is assumed to be laminar; if R_e is greater than 10,000, the flow is considered to be turbulent. Somewhere between 2000 and 10,000 the onset of turbulence begins.

In order to indicate the magnitude of the terms involved in the calculation of a Reynolds number, the calculation of the Reynolds number for water at 20°C in viscometer 1 is given:

d = 0.998 g/ml V = 3.10 cm^3
η = 0.0100 g/cm-sec j = 1.6 cm
t = 76.5 sec r = 0.03 cm

$$v = \frac{(3.10\ cm^3)}{(0.003\ cm)^2(76.5\ sec)} = 14.3\ cm/sec$$

$$R_e = \frac{(14.3 \text{ cm/sec})(0.998 \text{ g/cm}^3)(1.6 \text{ cm})}{(0.0100 \text{ g/cm-sec})} = 2280$$

For viscometer 2 the R_e value was 1980. At the other extreme the 45% sucrose solution at 20°C, which was used in the calibration of the viscometers, had R_e values for viscometers 1 and 2 of 38.0 and 33.1 respectively. The liquids used in calibrating the viscometers were within the range of Reynolds numbers indicating laminar flow. However, the NaOH and KOH solutions covered a broader viscosity range. The most viscous solution was the approximately 12 N NaOH solution at 25.0°C. The R_e values for it in the two viscometers used were 14.0 and 12.2. The least viscous solution was the approximately 2 N NaOH solution at 75.0°C; the R_e values for it for the two viscometers were 7500 and 6540. Therefore, for a few solutions of low concentration at high temperatures, the onset of turbulence may have begun. Had a viscometer with a larger efflux time been available, it would have been better to use it instead of the present ones. Generally for most of the liquids involved, it can be said they were undergoing laminar flow.

A Newtonian liquid is thought of as a simple liquid or a true liquid. A more detailed definition describes it as being a substance which will flow under the influence of any finite shearing stress, for which the rate of shear at any point is proportional to the shearing stress at that point, and for which the ratio of shearing stress to rate of shear is determined solely by its composition, temperature, and pressure (4). One can not speak of any liquid as being Newtonian or non-Newtonian as such, because its behavior could change with its

temperature or pressure. A good example of this is the liquefaction or solidification of butter and water. If H. Eyring's theory for the viscosity of liquids is followed, all liquids should be considered non-Newtonian (2). It is, however, only under high rates of shear that any effects are observable. One result that Eyring's theory leads to is the fact that fluid flow is Newtonian in all normal liquids of low molecular weight under reasonably attainable experimental conditions (2). It is, therefore, safe to assume that the liquids being investigated were Newtonian under the conditions of the determinations.

Most of the terms in the viscosity equation are dimensions of the viscometer, and they are very difficult to measure directly or accurately. An indirect method that can be used to accurately determine these grouped terms is given by the following rearrangement of the viscosity equation:

$$\eta/d = At - mB/t$$

where $A = \dfrac{\pi ghr^4}{8V(1 + nr)}$ and $B = \dfrac{V}{8\pi(1 + nr)}$

If the kinetic energy term, mB/t, is negligibly small, A can easily be calculated from the efflux time and the density of a standard solution of known viscosity. It is important to choose a liquid that can be accurately prepared so its viscosity is accurately known.

If the kinetic energy term can not be neglected, other means of determining A and B must be used. If the kinetic energy term is small compared to the Poiseuille part of the viscosity equation, mB can be

considered a constant. Likewise, the term, n, in the expression, $(1 + nr)$, can be set equal to zero if the 1/r ratio is high. The 1/r ratios for the two viscometers are 333 and 400 respectively. The ratios were considered to be high enough to consider n to be equal to zero.

There are two different methods of evaluating A and B. First, two different liquids of accurately known viscosity and density can be placed in the viscometer and their efflux times measured. Two equations containing two unknowns are then obtained. Simultaneous solution of these two equations gives the evaluation of the two constants. For one calibration run with the sucrose solution at 20.0°C, the following results were obtained:

	Viscometer 1	Viscometer 2
20% and 30% sucrose solutions		
A	$0.000131761\ cm^2/sec^2$	$0.000106750\ cm^2/sec^2$
B	$0.013196\ cm^2$	$0.021755\ cm^2$
30% and 40% sucrose solutions		
A	$0.000131778\ cm^2/sec^2$	$0.000106800\ cm^2/sec^2$
B	$0.013994\ cm^2$	$0.025235\ cm^2$
40% and 45% sucrose solutions		
A	$0.000131832\ cm^2/sec^2$	$0.000107059\ cm^2/sec^2$
B	$0.022322\ cm^2$	$0.087026\ cm^2$

If the kinetic energy correction is very small, η/d is approximately proportional to t, and the difference between the two ratios in the

numerator of the expression for mB,

$$mB = \frac{(\eta_1/d_1t_1) - (\eta_2/d_2t_2)}{(1/t_2)^2 - (1/t_1)^2}$$

is small and is influenced unduely by minor errors and uncertainties in η/d and t. The simultaneous solution of the two equations affords a poor measure of mB.

A more satisfactory evaluation of mB may result from assuming m = 1 and n = 0, and then calculating B from the dimensions of the viscometer. After the above substitutions were made,

$$B = \frac{V}{8\pi l} .$$

The volume, V, was measured by adding water from a burette, and slowly drawing it into the upper fiducial bulb. When the volume was added that just filled the marks between a and b, the value was recorded. The values for B for the two viscometers were 0.01233 cm^2 and 0.008157 cm^2. A value for A can now be calculated by using just one reference liquid of accurately known viscosity and density. In order to minimize the effect of the kinetic energy term, the efflux time should be fairly long. For the same calibration run as before, the values of A are:

Solution	Viscometer 1	Viscometer 2
20% sucrose	A = 0.000131715 cm^2/sec^2	A = 0.000106275 cm^2/sec^2
30% sucrose	A = 0.000131743 cm^2/sec^2	A = 0.000106558 cm^2/sec^2
40% sucrose	A = 0.000131768 cm^2/sec^2	A = 0.000106728 cm^2/sec^2
45% sucrose	A = 0.000131803 cm^2/sec^2	A = 0.000106911 cm^2/sec^2

As can be seen, the values of A stayed essentially constant over a wide range of Reynolds numbers. To check the validity of the assumption that the kinetic energy term is small compared to the Poiseuille term, the ratio of At/Bt^{-1} showed how much larger the Poiseuille term is than the kinetic energy term. For viscometer 1 the ratio varied from 200 to 3760 for the calibrating liquids. For viscometer 2 the ratio varied from 414 to 7000. Indeed the assumption was valid and especially so for the higher concentrated solutions.

Because of the caustic nature of the solutions being tested, it was necessary to check the calibration of the viscometers from time to time to determine if any etching had occurred. The viscometers were recalibrated after every other series of determinations. The following results show the changes in A for both viscometers after the series of runs:

Calibration	Viscometer 1 (cm^2/sec^2)	Viscometer 2 (cm^2/sec^2)
original	A = 0.00013038	A = 0.00010587
after 25° and 35°C run	A = 0.00013091	A = 0.00010616
after 45° and 55°C run	A = 0.00013175	A = 0.00010662
after KOH and mixtures	A = 0.00013174	A = 0.00010637

Some etching has occurred, but because of the frequent calibrations, little error has resulted because of it.

The viscosity of the solutions decreased as the temperature increased. For a 40% sucrose solution the viscosity can change about fourfold for a temperature increase of 50°C. Therefore, it is important

that the solutions be kept at a constant temperature throughout the efflux time measurement. The amount of regulation needed can be shown in the following manner. The viscosity of a 40% sucrose solution at 20 and 25°C is 6.200 and 5.187 cp respectively. The difference in viscosity for this 5°C range is 1.013 cp. For a 0.01°C change the change in viscosity would be 0.002 cp, which is a 0.04% relative error in the viscosity. The ± 0.05°C regulation which was able to be maintained would cause a relative percent error of 0.20%. As the temperature increases, the change in viscosity decreases. Therefore, at 70 and 75°C where the viscosities of the 40% sucrose solution are 1.608 and 1.402 cp, the change in viscosity is 0.206 cp/5°C. For the ± 0.05°C regulation, the relative percent error is only 0.13%. Therefore, when the regulation could only be controlled by 0.10°C, the error in the viscosity determination did not increase appreciably.

Many workers feel it is necessary to calibrate their viscometers at each temperature they are working at. But the number of liquids which can be used to calibrate a viscometer at all these different temperatures is few. As will be shown here, any effects of thermal expansion of the viscometer are self compensating. Any adjustment needed is for the different rate of thermal expansion of the liquid from the viscometer material.

For an increase in temperature over the calibrating temperature, each linear dimension of the instrument is increased by a factor,

$$F = 1 + e(T_u - T_c)$$

where e = mean linear coefficient of thermal expansion of the material which the viscometer is made of

T_u = temperature at which the viscometer was used

T_c = temperature at which the viscometer was calibrated.

The volume of the fiducial bulb is a product of three dimensions, and is increased by a factor of F^3. The changes in A and B can be indicated as such:

$$A_u = \frac{\pi g(hF)(rF)^4}{8(VF^3)(1F + nrF)} = \frac{\pi g h r^4}{8V(1 + nr)} \quad F = A_c F$$

$$B_u = \frac{(VF)^3}{8\pi(1F + nrF)} = \frac{V}{8\pi(1 + nr)} \quad F^2 = B_c F^2$$

where A_u and A_c = A at the temperature used and calibrated

B_u and B_c = B at the temperature used and calibrated

The material a viscometer is made of is usually very resistant to thermal shock. Its e value is on the order of $3 \times 10^{-6}/^{\circ}C$. If a temperature range, $T_u - T_c$, of $100^{\circ}C$ is chosen, F is only 1.0003 or A_u is only 0.03% larger than A_c. This error was less than that caused by the temperature control of the constant temperature bath. It was felt that there was no need to calibrate the viscometer at every temperature it was used. There was only a $50^{\circ}C$ spread; this makes the error even less. Although the temperature effect on B was somewhat larger, the significance of B in the calculation did not warrant any correction. The correction would be too small to be observed.

Although the error due to the expansion of the viscometer is small, what about the error due to the expansion of the liquid in the

viscometer? There are two errors to consider. One is the error due to the temperature at which the viscometer was filled and the other is the error due to the temperature at which the viscosity was determined.

The volume of liquid in the viscometer when it was calibrated may be different if a volume of liquid is pipetted into the viscometer at a different temperature than that at which the viscometer was calibrated. The volume of charge that the viscometer will hold at the time of the determination can be related to its volume at the temperature at which it was calibrated by the following equation:

$$\dot{V}_1 = \dot{V}_c \left[1 + B(T_1 - T_c)\right]$$

where $\dot{V}_1$ and $\dot{V}_c$ = the volume of charge at the time of the determination and calibration

T_1 and T_c = the temperature of the charge at the time of the determination and calibration

B = the mean volume coefficient of thermal expansion for the viscometer material.

The volume of charge, $\dot{V}_s$, is that volume in the viscometer at T_c when the viscometer was filled at T_1. The volume, $\dot{V}_s$, can be related to the volume at calibration by the following expression:

$$\dot{V}_s = \dot{V}_c \left[\frac{1 + B(T_1 - T_c)}{1 + A(T_1 - T_c)}\right]$$

where $$A = \frac{(d_c/d_1) - 1}{T_1 - T_c}$$

d_c and d_1 - density of the liquid at the temperatue of calibration and filling.

Thus the error in the volume of charge is $\dot{V}_c - \dot{V}_s$, and for T_1 greater than T_c, the position of the lower meniscus will be lower than normal by $(\dot{V}_c - \dot{V}_s)/\pi R^2$, where R is the radius of the lower meniscus. As a consequence, h is increased by the lowering of the lower meniscus. The relative change in h is equal to

$$\frac{h_1 - h_c}{h_c} = \frac{\dot{V}_c - \dot{V}_s}{\pi R^2 h_c}$$

By substituting in the value for $\dot{V}_s$ and assuming that $A(T_1 - T_c)$ is very small, the expression for the relative change in h can be given by

$$\frac{h_1 - h_c}{h_c} = \frac{V_c}{\pi R^2 h_c} (A - B)(T_1 - T_c)$$

The lower meniscus radius can be approximated by the following expression:

$$R = \sqrt{\frac{V}{\pi S}}$$

where V = the volume of the lower bulb

S = the difference in the heights of the meniscus in the lower bulb when the upper meniscus is at the marks a and b

For viscometer 1 the relative change in h for a 10°C difference in temperature is:

$$R^2 = \frac{(5.3\ cm^3)}{(1.5\ cm)\pi} = 1.124\ cm^2$$

$$A = \frac{\frac{0.99820\ g/cm^3}{0.99565\ g/cm^3} - 1.00000}{(30^\circ C - 20^\circ C)} = 0.000256/^\circ C$$

$$\frac{h_1 - h_c}{h_c} = \frac{(5.00\ cm^3)(2.56 \times 10^{-4}/^\circ C - 9.9 \times 10^{-6}/^\circ C)(30^\circ C - 20^\circ C)}{(1.124\ cm^2)(13.3\ cm)}$$

$$= 2.63 \times 10^{-4}$$

The relative percent error was $2.63 \times 10^{-2}\%$. For viscometer 2 the relative percent error was $6.77 \times 10^{-3}\%$. The values chosen were for a maximum difference that would occur between the temperature of calibration and the temperature at which the viscometer was filled. This error was again small compared to the error that was introduced from not being able to hold the temperature uniformly constant. No corrections were made for this error.

The correction for the temperature at which the determination was made is similar to the previous error discussion. Now the value of h can change due to the expansion of the liquid being different from the expansion of the viscometer material. The expression for the relative change in h from that at the calibration temperature is

$$\frac{h_1 - h_c}{h_c} = -\left[\frac{V_c(A - B) - e}{R^2 h}\right](T_u - T_c)$$

The temperatures ranged from a calibration temperature of $20^\circ C$ to a final determination at a temperature of $75^\circ C$. For viscometer 1, the relative error was calculated in the following manner:

$$A = \frac{\frac{0.99820\ g/cm^3}{0.97489\ g/cm^3} - 1.00000}{(75^\circ C - 20^\circ C)} = 0.0004347/^\circ C$$

$$\frac{h_1 - h_c}{h_c} = - \frac{5.00\ cm^3(4.347 \times 10^{-4}/^\circ C - 9.9 \times 10^{-6}/^\circ C) - 3.3 \times 10^{-6}/^\circ C}{\pi(1.124\ cm^2)(13.3\ cm)(75^\circ C - 20^\circ C)^{-1}}$$

$$= - 2.30 \times 10^{-3}$$

The relative percent error was $2.30 \times 10^{-1}\%$. For viscometer 2 the relative percent error was $4.59 \times 10^{-2}\%$. As can be seen, this is an important consideration at the higher temperatures of determination. The overall importance of this error will be discussed in a summary of important errors at the end of this section.

Liquids flowing through a small capillary will be subject to large amounts of resistance to flow. As a result of this friction, heat is generated. This increases the temperature of the liquid over that temperature at which it is being thermostatically controlled. If the kinetic energy correction is small, the mean temperature rise over the entire length of the capillary tube assuming adiabatic conditions is

$$\Delta T = 1.17 \times 10^{-5}\ h/c$$

where c = the specific heat of the liquid being studied.

For the solutions studied the specific heat is approximately 0.9 cal/g°C (52). For viscometer 1

$$\Delta T = \frac{(1.17 \times 10^{-5}\ cal/g\text{-}cm)(13.3\ cm)}{(0.9\ cal/g^\circ C)} = 1.7 \times 10^{-4\circ}C$$

For viscometer 2, $\Delta T = 1.6 \times 10^{-4\circ}C$. These are extremely small changes in temperature. Since the baths were only capable of control of $\pm 0.05^\circ C$, this error was regarded as being negligible.

As in density determinations, the effect due to the acceleration of gravity must be considered. But even if the viscometers were calibrated in one place and used in another, it would not be necessary to recalibrate the viscometers, since the new constant, A_u, can be calculated from the calibrated constant, A_c, by the following relationship:

$$A_u = A_c(g_u/g_c)$$

where g_u and g_c = the acceleration due to gravity where the viscometers were used and calibrated.

Since the viscometers were calibrated and used in the same place, there was no need to apply any corrections to the constants.

Is the volume of liquid draining from the upper fiducial bulb constant for liquids of different viscosity? In experiments conducted by the National Bureau of Standards they have confirmed that if the rates of flow from the fiducial bulb are proportional to the kinematic viscosity of the liquids, the volume delivered by the bulb is a constant, at least for a wide range of viscosities (4). If the kinetic energy is small, this error is considered to be small in the normal use of the viscometer. If additional air pressure is used to increase or extend the range of the viscometer, this assumption can no longer be made. No additional air pressure was used to extend the range of the viscometers, and the kinetic energy term was small for both viscometers; therefore, this error was considered to be negligible.

Probably the most difficult parameter to measure, but the one causing a considerable error, is the alinement of the viscometer.

The value of h is altered if the viscometer is not vertically alined. Either the alinement can be adjusted each time a determination is made, or a sturdy mount that will give reproducible alinement every time can be used. Once the viscometer is in position, this mount should be sturdy enough to keep its alinement.

In the Ostwald type viscometer there are two types of errors that can be introduced when the viscometer is misalined. First there is a reduction in the effective height of h by the amount $h(1 - \cos\theta)$ where θ is the angle of misalinement from verticle. The second error comes from the change in the center of the lower surface by a horizontal distance of Δj. This produces an additional change in h of $\pm j \sin\theta$. The total error is the sum of the two individual errors, and can be represented as:

$$\Delta h = (1 - \cos\theta)h \pm j\sin\theta$$

or

$$\Delta h = h(1 - \cos\theta \pm jh^{-1}\sin\theta)$$

The change in h for a 1° misalinement in viscometer 1 is

$$\Delta h = [(1 - 0.99985) \pm (1.6 \text{ cm})(13.3 \text{ cm})^{-1}(0.01745)]\ 13.3 \text{ cm}$$

$$\Delta h = 0.0299 \text{ cm and } 0.0259 \text{ cm.}$$

The larger relative percent error in h was 0.23%. For viscometer 2 the larger relative percent error was 0.27%.

Because of the large error that could occur from even so small a misalinement as 1°, the viscometers were alined with a plumb bob each time a determination was made. The agreement of the values of A shows that the alinement could not have been too poor.

The last error to be discussed is that due to surface tension effects. The shape of the meniscus changes with a change of the surface tension. This results in a change in the value of h. There is no accurate method of calculating the error caused by this effect, but an approximation can be used to estimate the magnitude of this error on viscosity. One of the easier approximations (5) to use is

$$\% \text{ error} = \frac{200}{gh}\left[\frac{1}{R_1} - \frac{1}{R_2}\right]\left[\frac{T_{sc}}{d_c} - \frac{T_{sl}}{d_l}\right]$$

where R_1 and R_2 = radius of the upper and lower bulbs respectively

T_{sc} and T_{sl} = surface tension of the calibrating liquid and liquid sample.

d_c and d_l = densities of the calibrating liquid and the liquid sample.

This equation can be broken up into two parts; one part that is dependent on the dimensions of the viscometer and one part that is dependent on the properties of the solutions. The part that is dependent on the properties of the solutions is the same for both viscometers, but the part dependent on the viscometer dimensions is not. This was calculated for both viscometers, and was five times larger for viscometer 2 than for viscometer 1. Most of the difference was due to the differences of the upper and lower radii of the fiducial bulbs.

The surface tension and density of the 30% sucrose solution will be used as the reference liquid. For the NaOH solutions used, the maximum error that is possible for surface tension effects is 0.017% for viscometer 1 and 0.081% for viscometer 2. The range of known

surface tension values for the KOH solutions was limited enough, but from the values given, the percent error for these solutions was somewhat lower than those for the NaOH solutions. The surface tension effects present in the calibration of the viscometers would show up in the values of the constant, A. An average value of A was used, and therefore, the effect of the surface tension was also averaged over the range of solutions used.

The uncertainty in the density of the pure solution causes an uncertainty in the viscosity of the pure solutions also. By computing the maximum predicted error for the viscosity in the simplified expression used, the influence of the uncertainty of several of the terms could be estimated. The total uncertainty of the viscosity of the solutions had an average relative percent error of 0.5%. Of this the uncertainty in the constant, A, consisted of 0.35%. The other main errors were the uncertainty in the time and density. For the low concentrated solutions, the uncertainty in the efflux time was the larger of the two measurement errors, and for the more concentrated solutions, the uncertainty in the density was the larger error. The uncertainty in the density resulted in an uncertainty of only 0.01 to 0.05% in the viscosity of the solutions. The uncertainty in the time was just the reverse order.

The presence of the carbonates in the solutions will undoubtedly influence the viscosity of the solutions. Very little work has been done in this area. One work (53) showed that a large carbonate concentration will increase the viscosity by 40%, but the solutions

they were using contained more carbonate than hydroxide. It was felt that any uncertainty in the viscosity due to the carbonates would be small compared to other errors in the determination.

In summary, it was first shown that the three assumptions made to simplify the viscosity equation were valid. The Reynolds numbers showed that the flow of the liquids through the capillary tube was laminar. The one possible exception being the lower concentrated solutions at higher temperatures, where the Reynolds numbers indicated the onset of turbulence may be starting. The liquids used were considered to be Newtonian. The assumption that the layer of liquid next to the wall has a zero velocity is also commonly accepted.

Further calculations showed the necessity of including the kinetic energy term, and the justification of setting the correction to the length of the capillary, n, equal to zero. The dimensions of the viscometer could then be grouped together into two constants, which were evaluated by use of reference liquids.

There were certain errors that were so small that there was no need to be concerned with them. These were the change in the acceleration due to gravity, heat generated by the resistance to flow in the capillary tube, and the constant volume of liquid flowing from the upper fiducial bulb. By a mathematical treatment, it was shown that the constants did not change appreciably when the temperature at which the viscometer was used increased. Likewise, there was little error introduced by the filling of the viscometer over a ten degree range. There was some error introduced by the increase of the temperature of

the run over the calibration temperature, but this was only noticeable at the higher temperatures. The largest error due to temperature effects was due to the regulation. At the lower temperatures a regulation of $\pm$ 0.05°C could produce an error of 0.3% in viscosity, and at the higher temperature regulation of $\pm$ 0.10°C still produced an error of only a little more. This is due to the fact that the viscosity is not changing as fast at higher temperatures. The temperature regulation may have been better, but an estimate of 0.3% error due to the regulation and measurement of the temperature is conservative.

There may be some error due to misalinement of the viscometer, but its magnitude is not accurately known. An estimate of 0.1% may not be too far off. The viscometers were alined each time with a plumb bob, but in the process of measuring the viscosity, the viscometer could have been moved slightly. An error due to the surface tension of the different liquids may be of some significance in the second viscometer. At most, the error was only on the order of 0.1%.

Any errors due to etching of the capillary were taken care of by the frequent recalibrations of the viscometers. However, an error no greater than that of the temperature regulation may be present in the later part of the second run in a couple of the sets. Most of the etching seems to have occurred at the high temperatures. Little seems to have occurred at 25.0°C.

Using the KOH solutions as a typical run, the average deviation of all the determinations is 0.41%. In this run most of the average

deviations for the individual solutions were approximately 0.3%, but for the 13 N case it was 0.74%. This is not common, but part of this may be due to the solution itself. The higher concentrated solutions may have a tendency to absorb water at a faster rate than the solutions of lower concentrations.

As a concluding observation the accuracy of the viscosity values could safely be assumed to be accurate to within a 0.5% limit.

Data and Curve Fitting

The experimental values of the density of the solutions studied are presented in Tables 1 and 2 along with the temperatures at which the measurements were made. The values for the density of the NaOH solutions at 55.0°C, 65.0°C, and 75.0°C were obtained by calculations in the manner described earlier.

It was not possible to make a direct comparison of the values of the density of the NaOH and KOH solutions with those reported in the International Critical Tables (14) or in papers by G. Akerlof and coworkers (15, 16), because the densities were determined at different temperatures. A comparison of the density values reported by M. A. Klochke and M. M. Godneva (18) with those of this work is shown in Figure 2. Good agreement was obtained except for one reported value which appears to be questionable.

As can be seen from Figure 2, the concentration dependence of the density is not linear. By plotting $(d-d_o)/N$ versus $N^{\frac{1}{2}}$, a straight line can be obtained as is shown in Figure 3. This relationship is known as the Root equation. In its more common form the Root equation is given as $d = d_o + AN + BN^{3/2}$. By a method of least squares calculations, the empirical constants A and B were evaluated. The results of these calculations are presented in Tables 3 through 9. As can be seen from the tables, the error in the calculated values is only slightly greater than the experimental error. The Root equation, therefore, affords an adequate description of the concentration dependence of the density when concentration is expressed in normality units.

Table 1. Density and Viscosity of the Sodium Hydroxide Solutions at Various Temperatures

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C	75.0°C
0.000	Density[a]	0.997075	0.994063	0.990244	0.985723	0.980580	0.974871
	Viscosity[b]	0.8913	0.7203	0.5970	0.5049	0.4346	0.3791
2.068	Density	1.08123	1.07675	1.07202	1.06683	1.06128	1.05548
	Viscosity	1.391	1.116	0.9191	0.7711	0.6602	0.5735
4.211	Density	1.15674	1.15163	1.14620	1.14059	1.13480	1.12875
	Viscosity	2.354	1.823	1.466	1.203	1.008	0.8617
6.305	Density	1.22268	1.21706	1.21134	1.20540	1.19920	1.19287
	Viscosity	4.062	3.017	2.331	1.851	1.516	1.265
8.379	Density	1.28249	1.27670	1.27057	1.26433	1.25784	1.25077
	Viscosity	7.064	4.959	3.678	2.813	2.227	1.812
10.366	Density	1.33466	1.32848	1.32198	1.31548	1.30884	1.30210
	Viscosity	11.631	7.714	5.455	4.043	3.091	2.447
12.250	Density	1.37990	1.37341	1.36653	1.35984	1.35311	1.34632
	Viscosity	17.872	11.195	7.608	5.447	4.064	3.144

[a]Density is in grams per milliliter.

[b]Viscosity is in absolute viscosity expressed in centipoises.

Table 2. Density and Viscosity of the Pure Solutions and the Mixtures at 25.0°C

	NaOH	2:1	1:1	1:2	KOH
Normality	0.000	0.000	0.000	0.000	0.000
Density[a]	0.997075	0.997075	0.997075	0.997075	0.997075
Viscosity[b]	0.8913	0.8913	0.8913	0.8913	0.8913
Normality	2.068	2.163	2.214	2.268	2.383
Density	1.08123	1.08968	1.09386	1.09810	1.10719
Viscosity	1.391	1.320	1.283	1.237	1.164
Normality	4.211	4.344	4.414	4.486	4.638
Density	1.15674	1.17083	1.17771	1.18503	1.19989
Viscosity	2.354	2.058	1.921	1.795	1.548
Normality	6.305	6.497	6.598	6.702	6.920
Density	1.22268	1.24298	1.25336	1.26401	1.28605
Viscosity	4.062	3.272	2.943	2.637	2.127
Normality	8.379	8.574	8.674	8.777	8.991
Density	1.28285	1.30747	1.32018	1.33316	1.35986
Viscosity	7.064	5.184	4.499	3.873	2.961
Normality	10.366	10.624	10.724	10.849	11.108
Density	1.33466	1.36599	1.38208	1.39843	1.43191
Viscosity	11.631	8.116	6.864	5.864	4.352
Normality	12.250	12.563	12.725	12.892	13.239
Density	1.37990	1.41846	1.43830	1.45865	1.50010
Viscosity	17.872	12.370	10.492	8.977	6.770

[a]Density is in grams per milliliter.

[b]Viscosity is absolute viscosity expressed in centipoises.

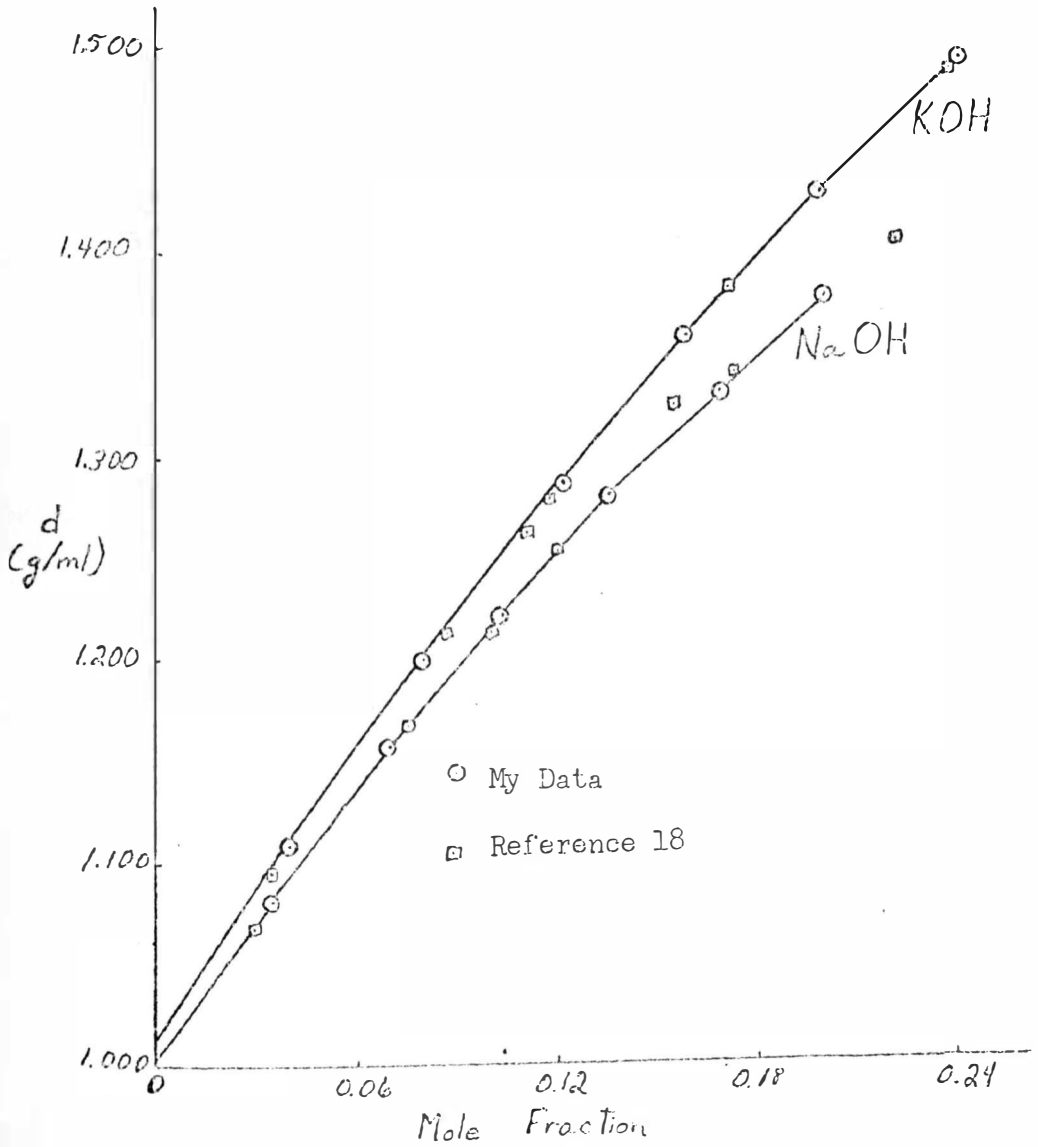


Figure 2. Comparisons of the density of NaOH and KOH solutions at 25.0°C with other works

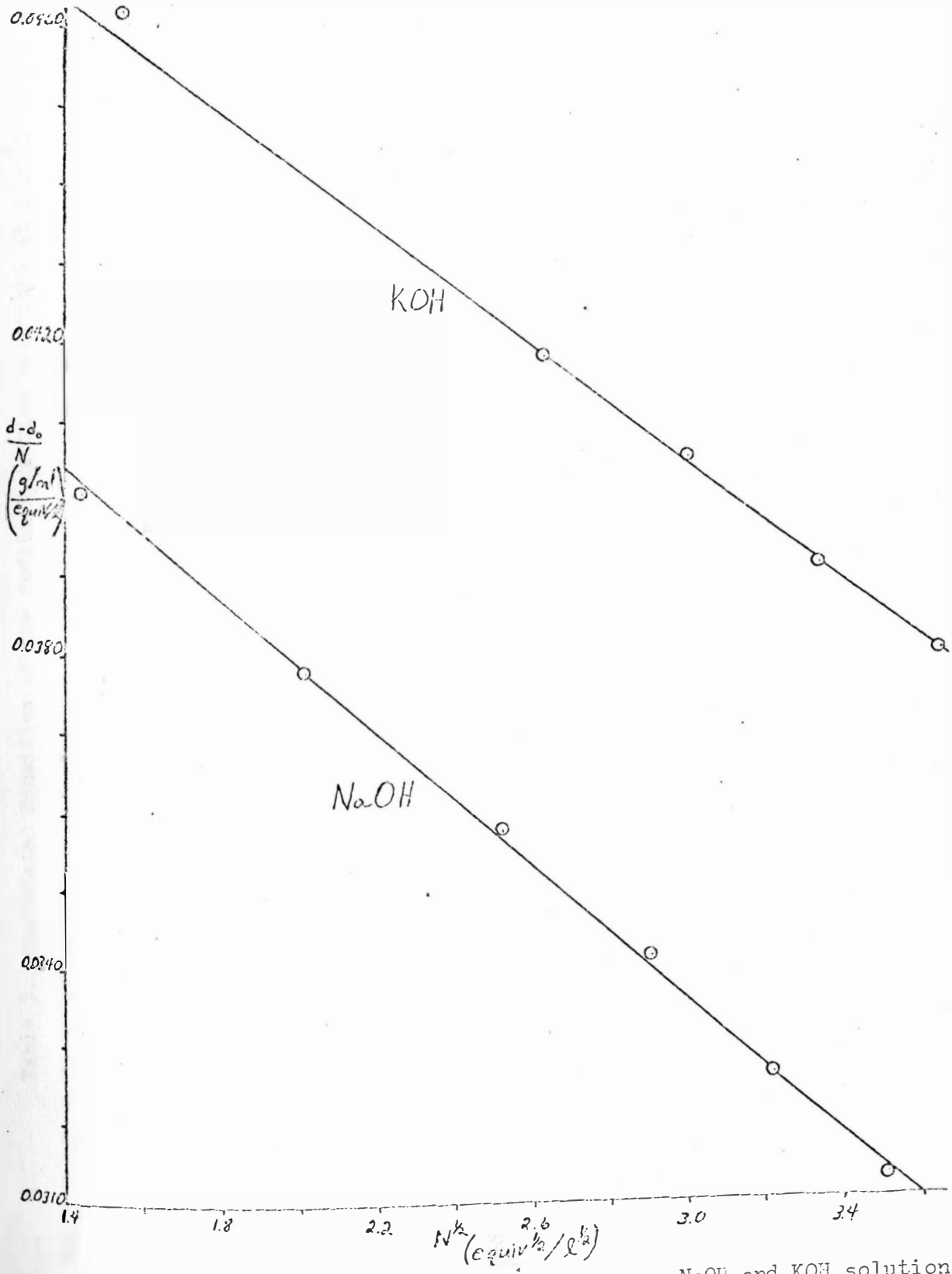


Figure 3. Relation of $(d - d_o)/N$ and $N^{\frac{1}{2}}$ of Aqueous NaOH and KOH solutions at 25.0°C

Table 3. Calculated Densities of the Sodium Hydroxide Solutions at 25.0°C

	Concentration	Density Exp. (g/ml)	Density calc.[a] (g/ml)	% Error	Density calc.[b] (g/ml)	% Error
Normality	0.000	0.997075	0.997075	0.000		
Mole Fraction	0.00000				0.997075	0.000
Normality	2.068	1.08123	1.081261	0.003		
Mole Fraction	0.03597				1.081173	0.005
Normality	4.211	1.15674	1.156648	0.008		
Mole Fraction	0.07128				1.156912	0.015
Normality	6.305	1.22268	1.222782	0.008		
Mole Fraction	0.10478				1.222905	0.018
Normality	8.379	1.28249	1.282324	0.013		
Mole Fraction	0.13745				1.282093	0.031
Normality	10.366	1.33466	1.334550	0.008		
Mole Fraction	0.16874				1.334268	0.029
Normality	12.250	1.37990	1.380162	0.019		
Mole Fraction	0.19871				1.380345	0.032

[a] Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.04728727$ $B = -0.00457579$

[b] Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.997075$ $A = 2.4395073762$ $A' = 0.89179612$ $B = 1.18215407$

Table 4. Calculated Densities of the 2:1 Mixture Solutions at 25.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density calc.[b] (g/ml)	% Error
Normality	0.000	0.997075	0.997075	0.000		
Mole Fraction	0.00000				0.997075	0.000
Normality	2.163	1.08968	1.089557	0.011		
Mole Fraction	0.03782				1.089374	0.028
Normality	4.344	1.17083	1.170881	0.004		
Mole Fraction	0.07439				1.171104	0.024
Normality	6.497	1.24298	1.243541	0.045		
Mole Fraction	0.10988				1.243779	0.064
Normality	8.574	1.30747	1.307785	0.024		
Mole Fraction	0.14396				1.307785	0.024
Normality	10.602	1.36599	1.365767	0.016		
Mole Fraction	0.17752				1.365624	0.027
Normality	12.563	1.41846	1.417759	0.050		
Mole Fraction	0.21057				1.417828	0.045

[a] Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.04932140$ $B = -0.00446762$

[b] Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.997075$ $A = 2.5497607722$ $A' = 0.93599954$ $B = 1.15762129$

Table 5. Calculated Densities of the 1:1 Mixture Solutions at 25.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density Calc.[b] (g/ml)	% Error
Normality	0.000	0.997075	0.997075	0.000		
Mole Fraction	0.00000				0.997075	0.000
Normality	2.214	1.09386	1.093671	0.017		
Mole Fraction	0.03883				1.093447	0.038
Normality	4.414	1.17771	1.177895	0.016		
Mole Fraction	0.07609				1.178121	0.035
Normality	6.598	1.25336	1.253967	0.048		
Mole Fraction	0.11265				1.254247	0.071
Normality	8.674	1.32018	1.320631	0.034		
Mole Fraction	0.14748				1.320734	0.042
Normality	10.724	1.38208	1.381768	0.023		
Mole Fraction	0.18228				1.381659	0.031
Normality	12.725	1.43830	1.437392	0.063		
Mole Fraction					1.438302	0.063

[a]Equation for normality: $D = D_o + AN + BN^{3/2}$ A = 0.05007877 B = -0.00433865

[b]Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

D_o = 0.997075 A = 2.5933666071 A' = 0.95295688 B = 1.13198421

Table 6. Calculated Densities of the 1:2 Mixture Solutions at 25.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density Calc.[b] (g/ml)	% Error
Normality	0.000	0.997075	0.997075	0.000		
Mole Fraction	0.00000				0.997075	0.000
Normality	2.268	1.09810	1.097931	0.015		
Mole Fraction	0.03990				1.097689	0.037
Normality	4.487	1.18503	1.185078	0.004		
Mole Fraction	0.07785				1.185280	0.022
Normality	6.702	1.26401	1.264670	0.052		
Mole Fraction	0.11557				1.265005	0.079
Normality	8.777	1.33316	1.333760	0.045		
Mole Fraction	0.15118				1.333964	0.060
Normality	10.849	1.39843	1.398161	0.019		
Mole Fraction	0.18733				1.398086	0.025
Normality	12.892	1.45865	1.457611	0.071		
Mole Fraction	0.22401				1.457472	0.081

[a]Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.05079658$ $B = -0.00419821$

[b]Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.997075$ $A = 2.6358598563$ $A' = 0.96920945$ $B = 1.11075227$

Table 7. Calculated Densities of the Potassium Hydroxide Solutions at 25.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density Calc.[b] (g/ml)	% Error
Normality	0.000	0.997075	0.997075	0.000		
Mole Fraction	0.00000				0.997075	0.000
Normality	2.383	1.10719	1.107002	0.017		
Mole Fraction	0.04223				1.106699	0.044
Normality	4.638	1.19989	1.199950	0.005		
Mole Fraction	0.08166				1.200142	0.021
Normality	6.920	1.28605	1.286796	0.058		
Mole Fraction	0.12192				1.287256	0.094
Normality	8.991	1.35986	1.360525	0.049		
Mole Fraction	0.15920				1.360916	0.078
Normality	11.108	1.43191	1.431549	0.025		
Mole Fraction	0.19838				1.431521	0.027
Normality	13.239	1.50010	1.498998	0.073		
Mole Fraction	0.23951				1.498620	0.098

[a] Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.05219249$ $B = -0.00392447$

[b] Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.997075$ $A = 2.7178586301$ $A' = 0.99984430$ $B = 1.08866735$

Table 8. Calculated Densities of the Sodium Hydroxide Solutions at 35.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density Calc.[b] (g/ml)	% Error
Normality	0.000	0.994063	0.994063	0.000		
Mole Fraction	0.00000				0.994063	0.000
Normality	2.068	1.07675	1.076882	0.012		
Mole Fraction	0.03597				1.076833	0.008
Normality	4.211	1.15163	1.151379	0.022		
Mole Fraction	0.07128				1.151649	0.002
Normality	6.305	1.21706	1.216980	0.007		
Mole Fraction	0.10478				1.2170818	0.002
Normality	8.379	1.27670	1.276259	0.035		
Mole Fraction	0.13745				1.2759881	0.056
Normality	10.366	1.32848	1.328447	0.002		
Mole Fraction	0.16874				1.3281128	0.028
Normality	12.250	1.37341	1.374197	0.057		
Mole Fraction	0.19871				1.374322	0.066

[a]Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.04633344$ $B = -0.00437213$

[b]Equation for mole fraction: $\ln(D - D_o) = A' + \ln X - BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.994063$ $A = 2.3967145331$ $A' = 0.87409885$ $B = 1.13278264$

Table 9. Calculated Densities of the Sodium Hydroxide Solutions at 45.0°C

	Concentration	Density Exp. (g/ml)	Density Calc.[a] (g/ml)	% Error	Density Calc.[b] (g/ml)	% Error
Normality	0.000	0.990244	0.990244	0.000		
Mole Fraction	0.00000				0.990244	0.000
Normality	2.068	1.07202	1.072170	0.014		
Mole Fraction	0.03597				1.072135	0.011
Normality	4.211	1.14620	1.145994	0.018		
Mole Fraction	0.07128				1.146265	0.006
Normality	6.305	1.21134	1.211099	0.020		
Mole Fraction	0.10478				1.211191	0.012
Normality	8.379	1.27057	1.270013	0.044		
Mole Fraction	0.13745				1.269728	0.066
Normality	10.366	1.32198	1.321954	0.002		
Mole Fraction	0.16874				1.321603	0.029
Normality	12.250	1.36653	1.367554	0.075		
Mole Fraction	0.19871				1.367660	0.083

[a]Equation for normality: $D = D_o + AN + BN^{3/2}$ $A = 0.04576129$ $B = -0.00427454$

[b]Equation for mole fraction: $\ln(D - D_o) = A' + \ln X + BX$ or $D - D_o = AX\exp(-BX)$

$D_o = 0.990244$ $A = 2.3696134366$ $A' = 0.862726840$ $B = 1.11331901$

The Root equation was tried using concentration expressed in mole fraction units. Errors, which greatly exceeded the experimental error, were obtained in the calculated results. An empirical equation, $d = A + Bc + Cc^2$ used by G. Janz and his coworkers (22), was tried, but similar results were obtained.

If $\log (d - d_o)$ is plotted versus the mole fraction of the solute, a slightly bowed line is obtained as can be seen in Figure 4. An exponential equation basically describes this behavior, but a term not included in the exponential part must be added to account for the slight bowing of the line. An equation of the type, $(d - d_o) = AX\exp(-BX)$, was tried where X is the concentration of the solute as mole fraction. The empirical constants, A and B, were found by a least squares method. The results obtained are presented in Tables 3 through 9. As can be seen the error is somewhat larger than that of the Root equation, but the results adequately describe the dependence. In logarithmic form this equation is $\log (d - d_o) = \log A + \log X - BX$.

The temperature dependence of the density of the NaOH solutions studied is given in Table 1. As can be seen in Figure 5, the temperature dependence of the density of the solutions is not linear over a broad range of temperatures. However, over small temperature ranges of not more than 20 to 30 degrees C, a linear approximation can be made, such as $d = dt_o - A(t - t_o)$ or $d = A - Bt$. For larger ranges a quadratic equation may be used (25). Two different types of quadratic equations were used on the present data. The first equation was

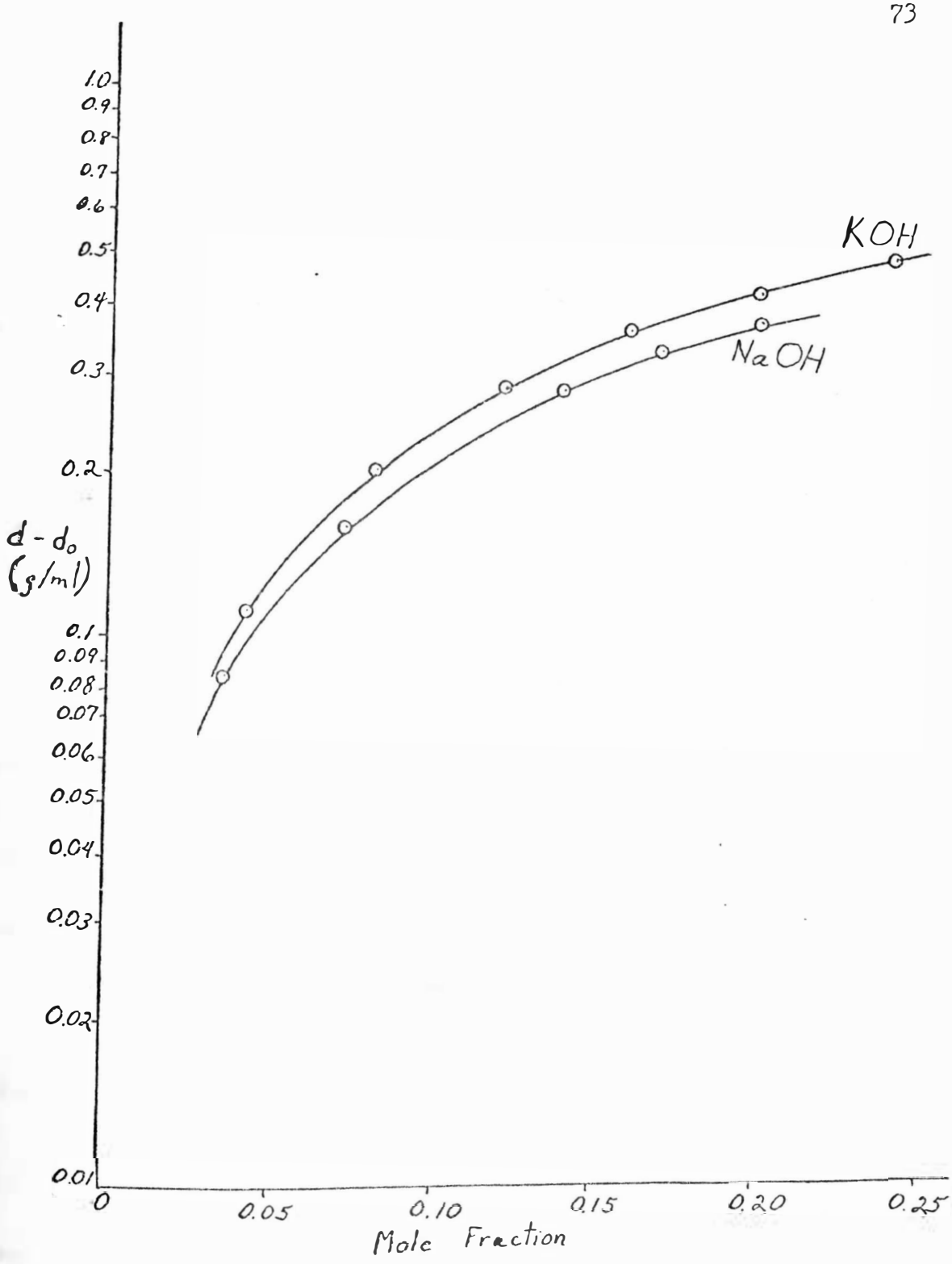


Figure 4. Relation of $\log(d - d_o)$ and concentration of aqueous NaOH and KOH solutions at 25.0°C

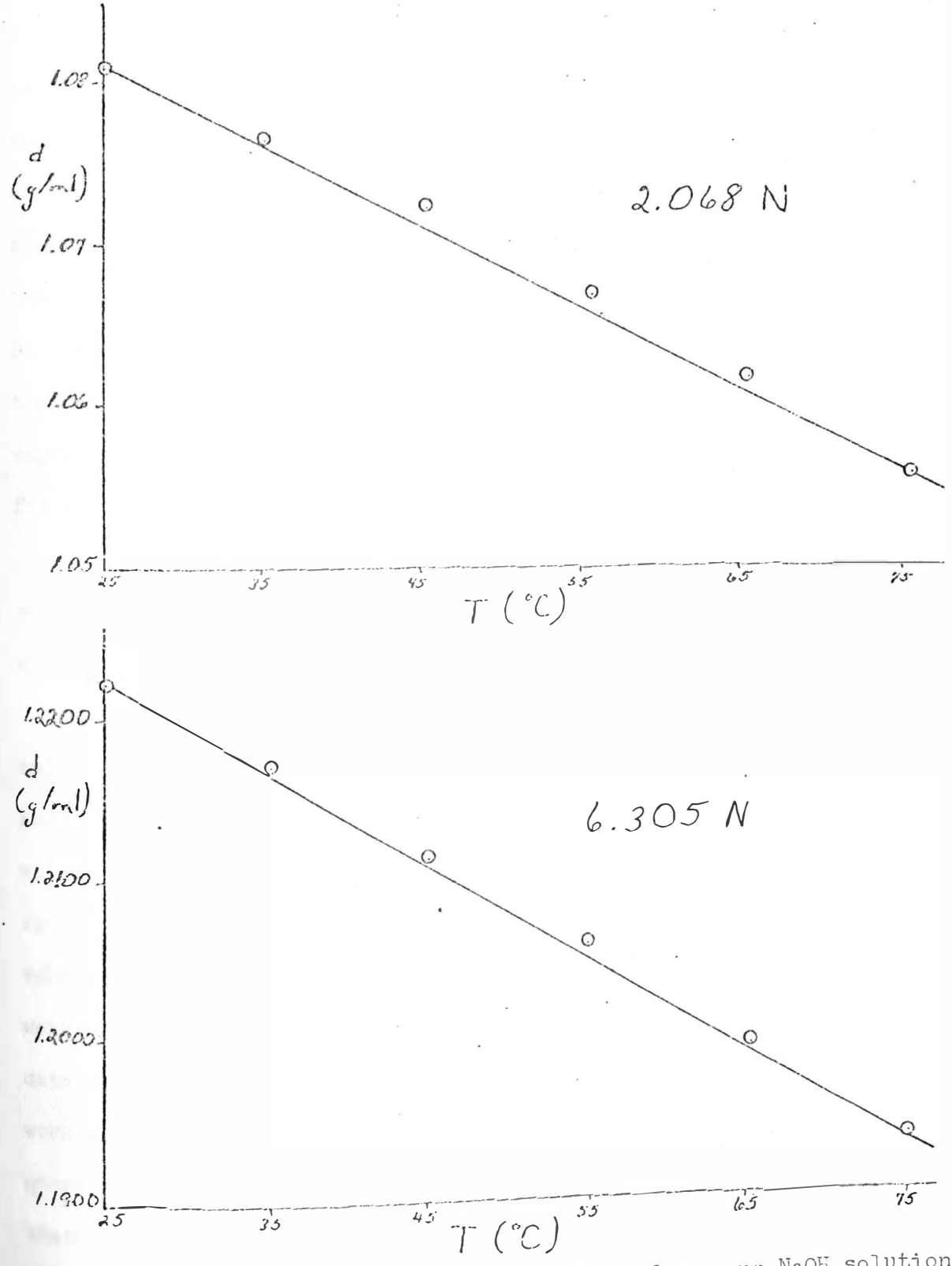


Figure 5. Relation of density and temperature of aqueous NaOH solutions for various concentrations

$d = d_{t_o} + Bt + Ct^2$ where d_{t_o} is the density of the solution at the lowest temperature in the interval and t is the temperature in ^{o}C at which the density was determined. The results obtained were within experimental error. However, by replacing d_{t_o} by an empirical constant such as Janz (22) does, the calculated densities were within 0.01% of the measured values. The final equation used is of the type, $d = A + Bt + Ct^2$, where A, B, and C are empirical constants and t is the temperature in ^{o}C. The results are presented in Table 10. The empirical constants A, B, and C were determined by a least squares fit of the density data.

The experimental values of the viscosities of the NaOH and KOH solutions studied are given in Tables 1 and 2 along with the temperatures at which they were determined.

By means of a viscosity-concentration graph, the viscosity values reported by Othmer and Silvis (17), Klochke and Godneva (18), and Baron and Matveeva (19) for these solutions can be compared to values determined in this work. Figure 6 shows a comparison of values at 25^{o}, 50^{o}, and $75^{o}C$ for the NaOH solutions. As can be seen, the values of Baron and Matveeva are somewhat higher than those of this work while the values of Othmer and Silvis are somewhat lower. The data reported by Klochke and Godneva is irregular compared to this work and that of the others; therefore its reliability can be questioned. A couple of points should be clarified here. One is that Othmer and Silvis reported their data in the form of a nomograph, thus the values plotted are only approximate values. Also my data for

Table 10. Temperature Dependent Equations for the Density of the Sodium Hydroxide Solutions for Various Concentrations[a]

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C	75.0°C
2.068	Density Exp.	1.08123	1.07675	1.07202	1.06683	1.06128	1.05548
	Density Calc.[b]	1.081211	1.076780	1.071988	1.066836	1.061324	1.055451
	% Error	0.0018	0.0028	0.0029	0.0006	0.0041	0.0028
4.211	Density Exp.	1.15674	1.15163	1.14620	1.14059	1.13480	1.12875
	Density Calc.[c]	1.156740	1.151595	1.146222	1.140622	1.134793	1.128737
	% Error	0.0000	0.0030	0.0019	0.0028	0.0006	0.0011
6.305	Density Exp.	1.22268	1.21706	1.21134	1.20540	1.19920	1.19287
	Density Calc.[d]	1.222648	1.217097	1.211342	1.205384	1.199222	1.192857
	% Error	0.0026	0.0030	0.0002	0.0013	0.0018	0.0011
8.379	Density Exp.	1.28249	1.27670	1.27057	1.26433	1.25784	1.25077
	Density Calc.[e]	1.282455	1.276700	1.270660	1.264335	1.257723	1.250826
	% Error	0.0027	0.0000	0.0071	0.0004	0.0092	0.0045
10.366	Density Exp.	1.33466	1.32848	1.32198	1.31548	1.30884	1.30210
	Density Calc.[f]	1.334691	1.328411	1.322010	1.315490	1.308849	1.302089
	% Error	0.0024	0.0052	0.0023	0.0007	0.0007	0.0009
12.250	Density Exp.	1.37990	1.37341	1.36653	1.35984	1.35311	1.34632
	Density Calc.[g]	1.379948	1.373288	1.366595	1.359867	1.353104	1.346308
	% Error	0.0035	0.0089	0.0047	0.0020	0.0004	0.0009

[a] Equation for degrees Centigrade: $D = A + Bt + Ct^2$

[b] $A = 1.09070999$ $B = -0.0003348990$ $C = -0.0000018030$

[c] $A = 1.16860675$ $B = -0.0004461965$ $C = -0.0000011386$

[d] $A = 1.23563498$ $B = -0.0004940280$ $C = -0.0000010180$

[e] $A = 1.29559192$ $B = -0.0004897806$ $C = -0.0000014279$

[f] $A = 1.34986762$ $B = -0.0005920468$ $C = -0.0000006001$

[g] $A = 1.39644649$ $B = -0.0006556600$ $C = -0.0000001714$

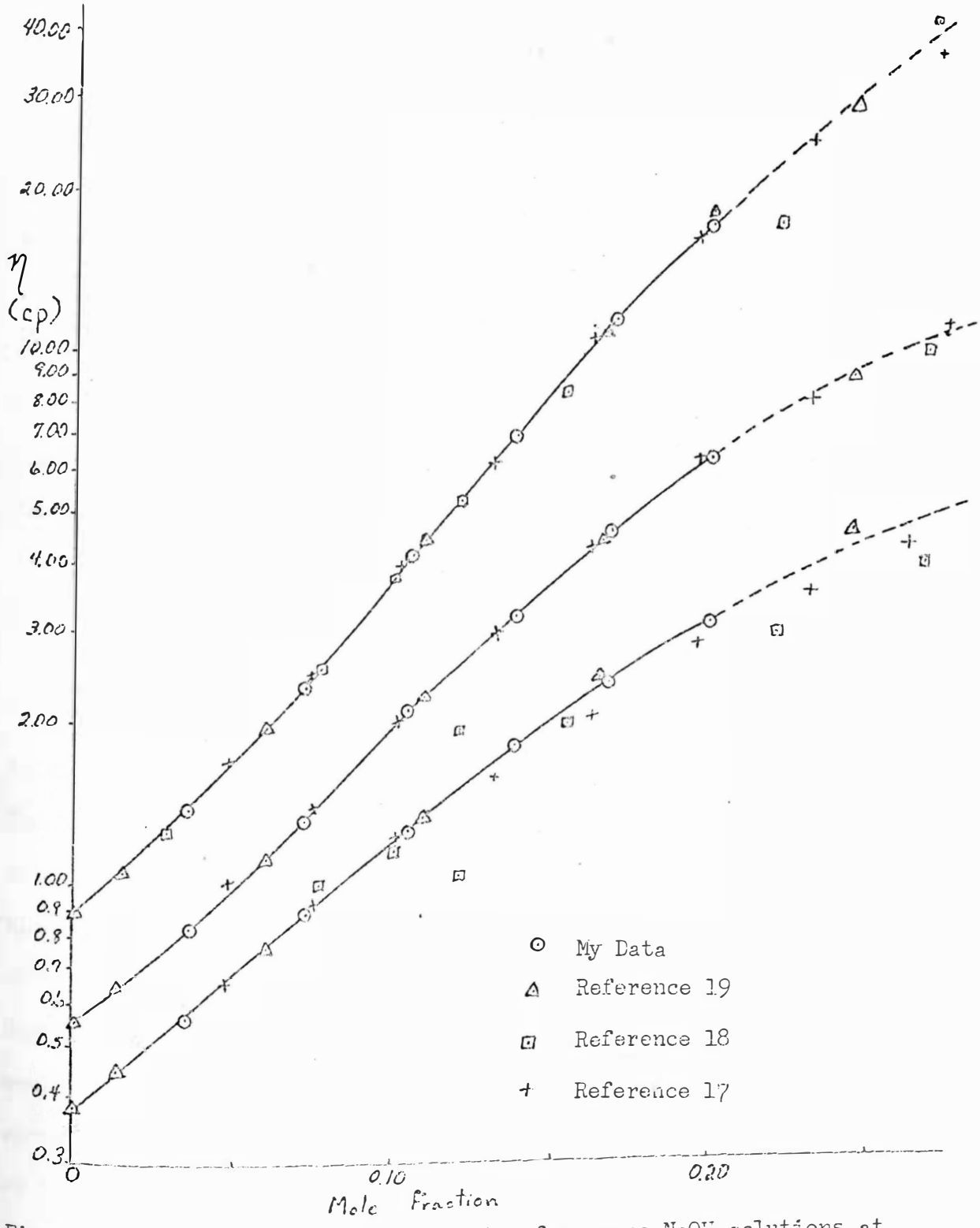


Figure 6. Comparisons of the viscosity of aqueous NaOH solutions at various temperatures with other works

50°C are calculated data. It will be shown shortly that the values are accurate within experimental error.

A comparison of the viscosity values of the KOH solutions is presented in Figure 7. The agreement between the values given by Klochke and Godneva (18) and this work is very good.

The complexity of the $\ln\eta$ versus concentration curve for NaOH at 25° was noted previously by Baron and Matveeva (19), but as can be seen in Figure 8, the complexity diminishes as the temperature increases. The complexity of the curve is believed to be caused by changes in the water structure that occur as the concentration of the electrolyte increases. This complexity is not so prevalent in the KOH solutions and is reduced in the solutions of the mixtures of the two electrolytes, as can be seen in Figure 9.

Due to the complexity of the $\ln\eta$ versus concentration curve, it is difficult to find an equation which describes this relationship. The Dole-Jones equation and its modifications can not be expected to hold for these solutions, because of the exceedingly high concentrations involved. A plot of $(\eta/\eta_o - 1)/N^{\frac{1}{2}}$ versus $N^{\frac{1}{2}}$ in Figure 10 clearly shows that the relationship is not linear. The equations used by H. Hagnas (20) may have worked but it was felt a simpler relationship could be found. The viscosity-concentration relationship for solutions above the Einstein region proposed by S. G. Moulik (34) was tried, but as the plot in Figure 11 shows, the relationship is not linear as is predicted. Janz et al. (22) have proposed many viscosity-concentration equations, but they are as varied as the compounds used and the

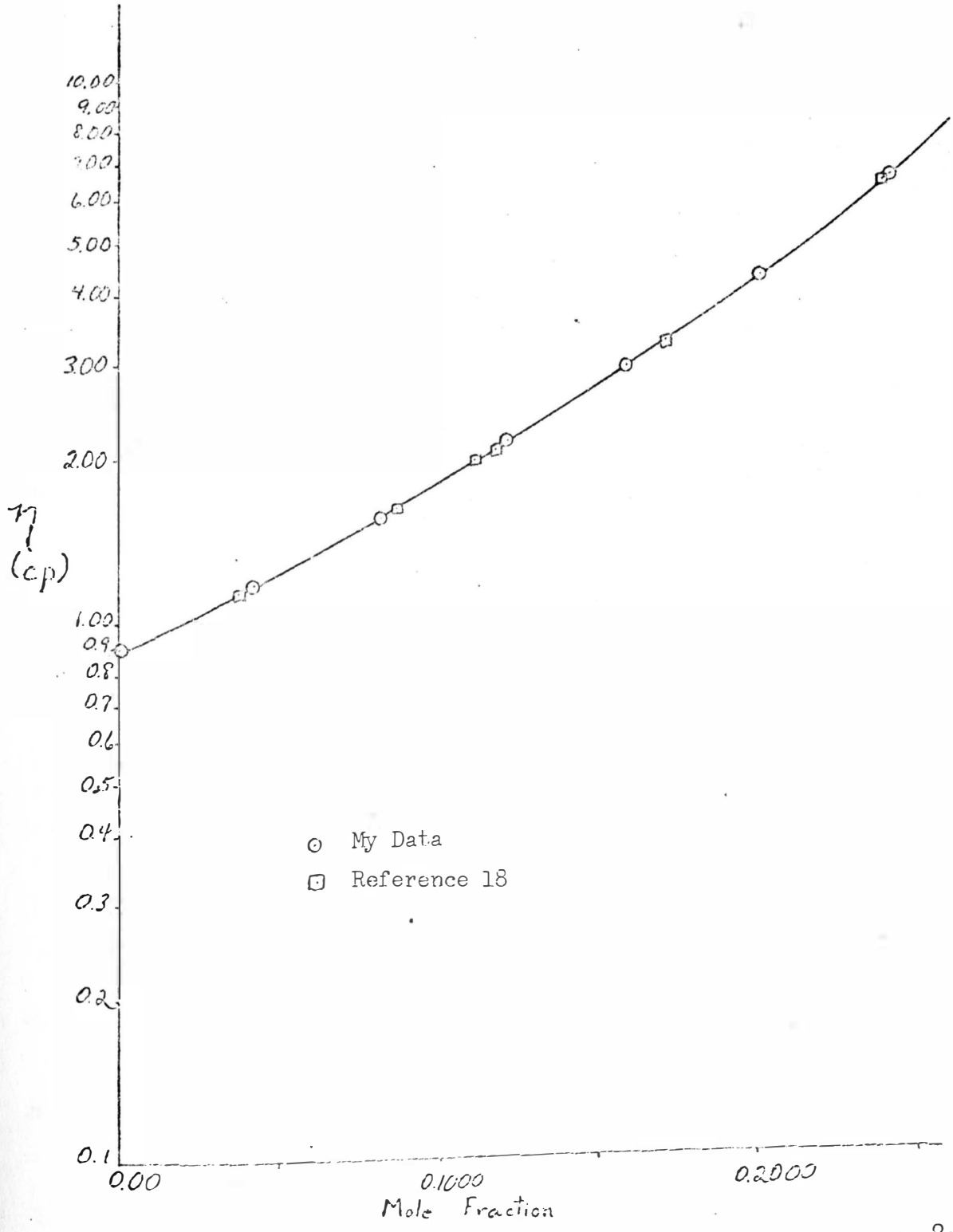


Figure 7. Comparisons of the viscosity of aqueous KOH solutions at 25.0°C with other works

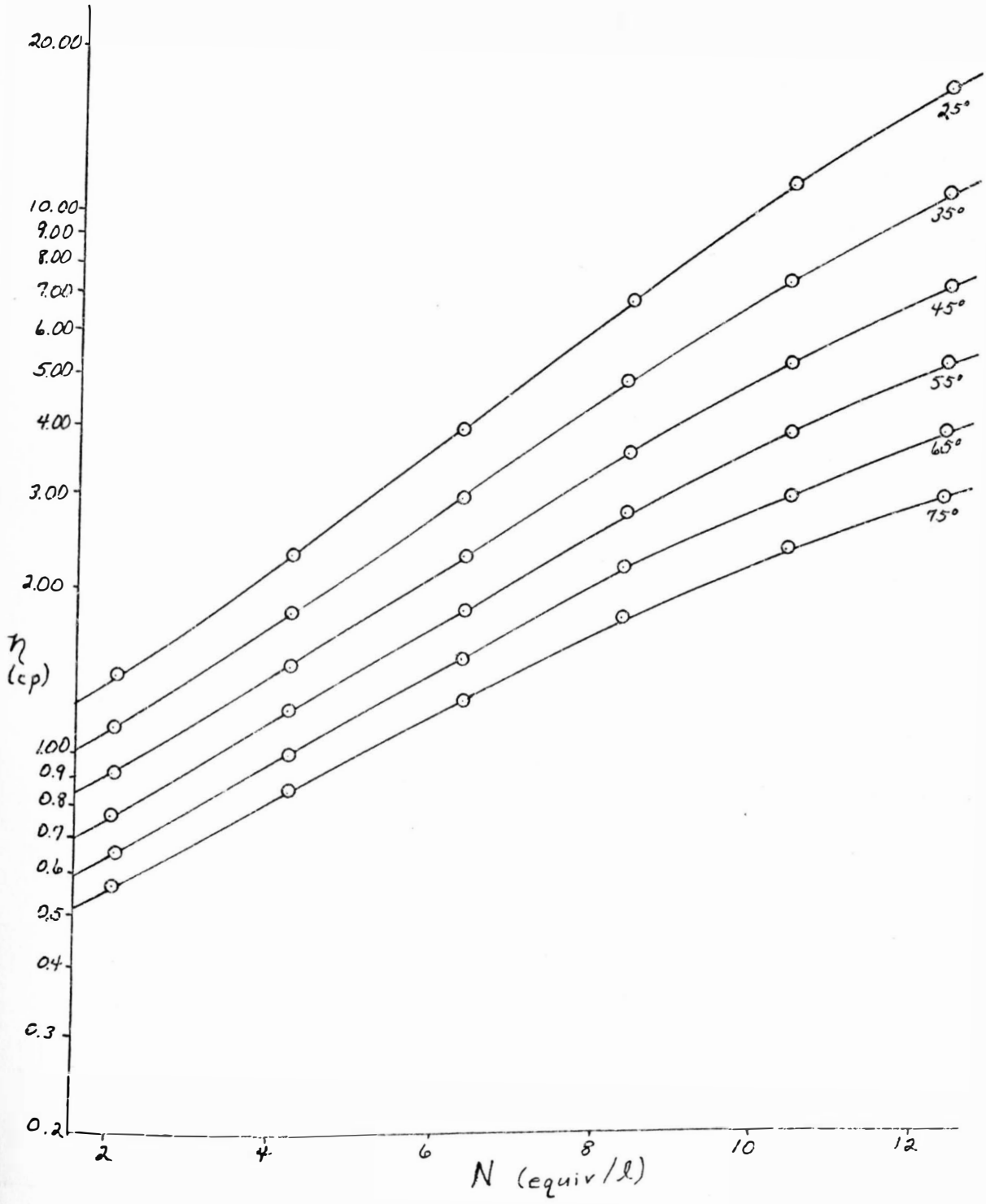


Figure 8. Relation of log η and concentrations of aqueous NaOH solutions at all temperatures under investigation

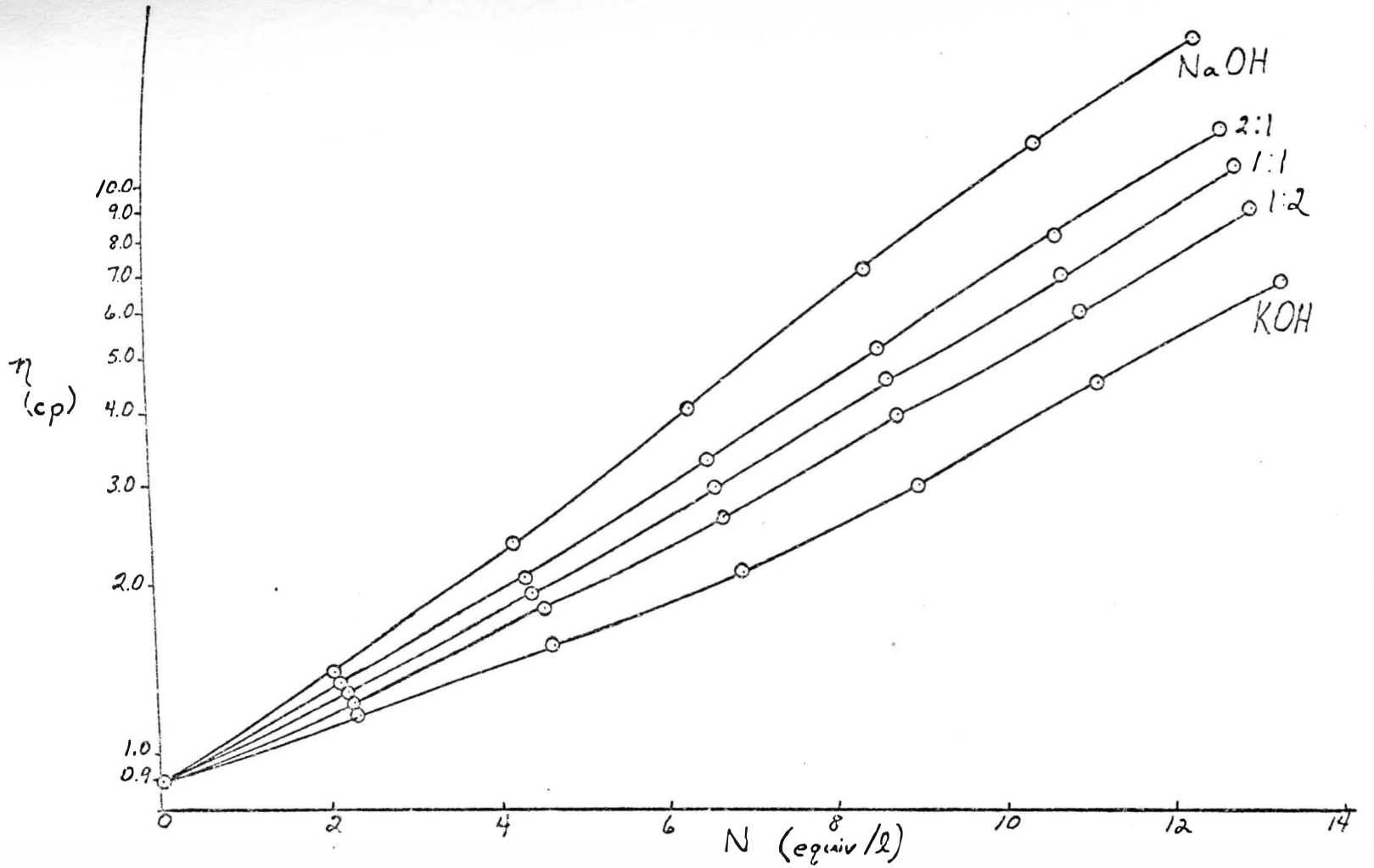


Figure 9. Relation of logη and concentrations of aqueous NaOH, KOH, and mixture solutions at 25.0°C

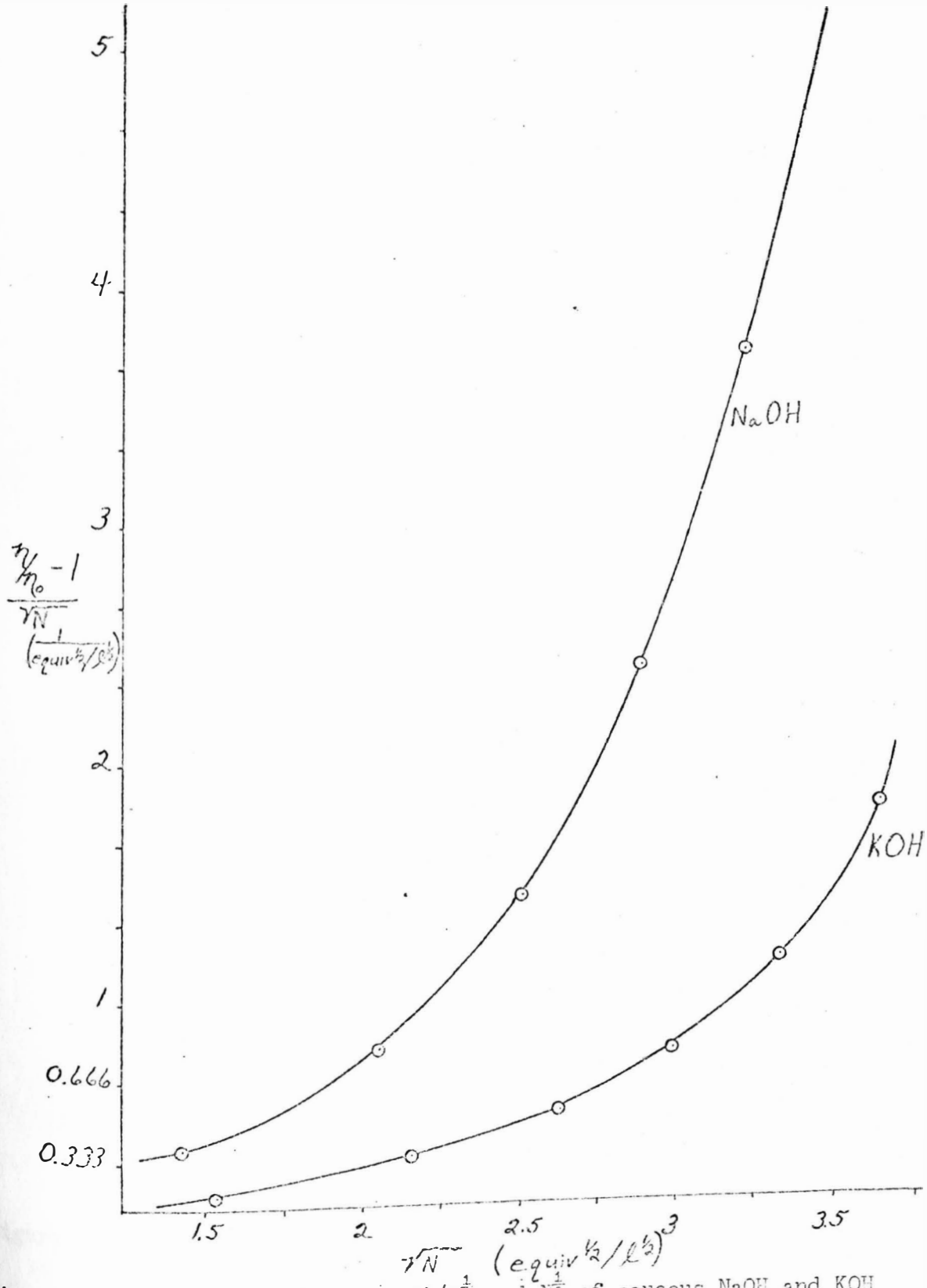


Figure 10. Relation of $(\eta/\eta_o - 1)/N^{\frac{1}{2}}$ and $N^{\frac{1}{2}}$ of aqueous NaOH and KOH solutions at 25.0°C

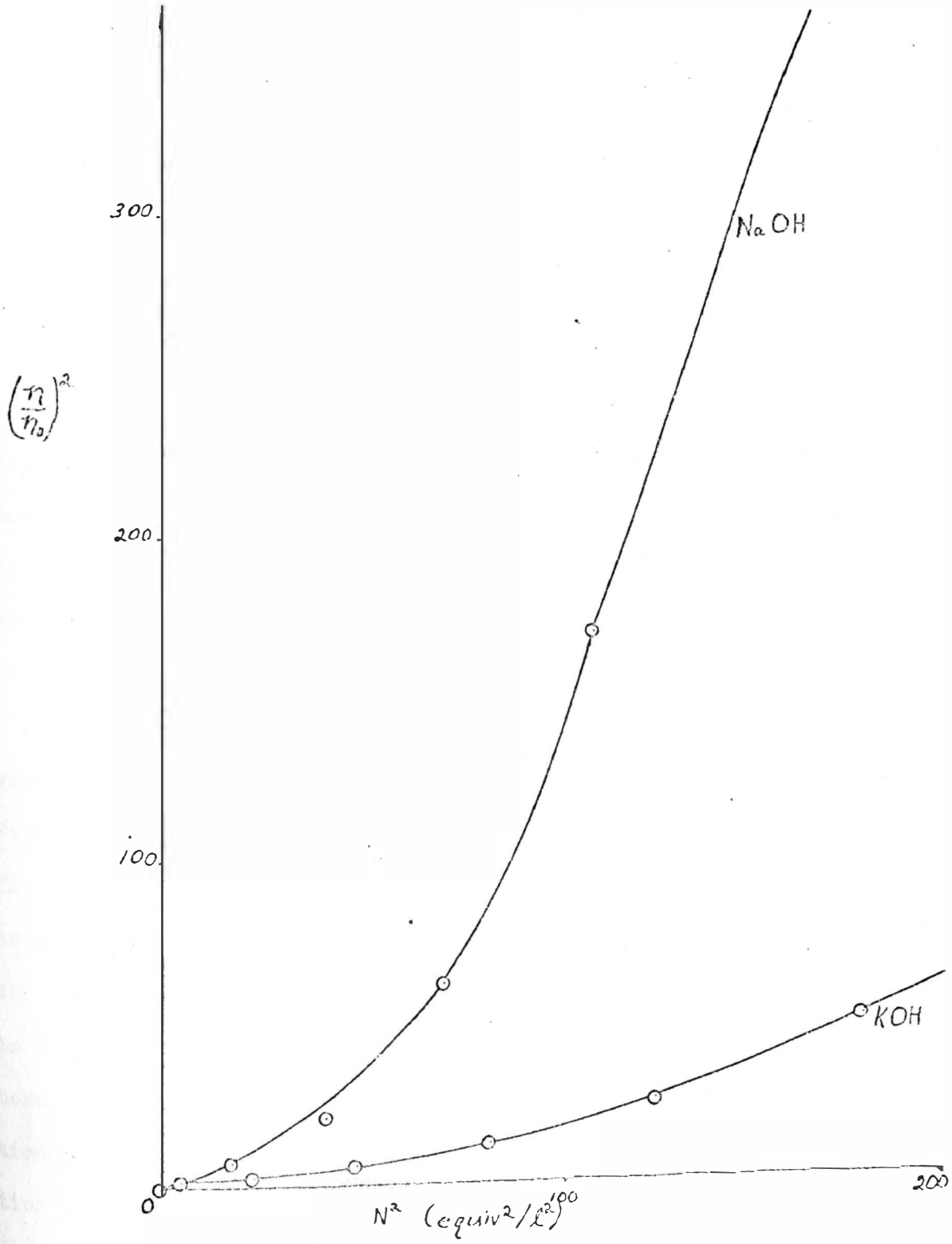


Figure 11. Relation of $(\eta/\eta_0)^2$ and N^2 of aqueous NaOH and KOH solutions at 25.0°C

concentration ranges tried. However, in earlier works (35), a simpler equation which was a function of the concentration to varying powers, showed promise. The equation, $\eta = \eta_o + AN + BN^2 + CN^3$, was tried and an accuracy of only $\pm$ 3% was obtained. Observing the plot of ln η versus concentration in Figures 8 and 9, it can be seen that a log type relationship may be feasible. A relationship of the type, $\eta = Ab^N$ was tried, but an accuracy of only $\pm$ 5% was obtained. Next a log function used by L. L. Ezrokli (33) was tried, but in a modified form. The equation used was $\ln\eta = \ln\eta_o + Ac + Bc^2 + Cc^3$. The results for concentration given in normality and mole fraction are presented in Tables 11 through 20. The accuracy achieved was within experimental error, less than $\pm$ 0.5%. The empirical constants, A, B, and C, were found by a least squares calculation of the viscosity data.

The Arrhenius relationship for the temperature dependence of the viscosity of the solutions was tried, but as Figure 12 shows for the NaOH solutions, the relationship is not linear. When a least squares fit to the data was made the calculated results from the equation were accurate to only $\pm$ 5%. Molten salt viscosity-temperature relationships are often represented by the Arrhenius type equation, but the equation is extended to a quadratic form or even cubic (25). This was not tried here. Instead, for the purpose of checking some theoretical considerations, a modification to the Fulcher equation was tried. The modification used was the one proposed by C. A. Angell (41) and C. T. Moynihan (39), in which $\eta = AT^{\frac{1}{2}}\exp(B/\ T - T_o)$. The empirical constants A, B, and T_o could not be solved for directly as in the usual least squares

Table 11. Calculated Viscosities of the Sodium Hydroxide Solutions at 25.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.8913	0.89130	0.00		
Mole Fraction	0.00000				0.9813	0.00
Normality	2.068	1.391	1.3903	0.05		
Mole Fraction	0.03597				1.3890	0.14
Normality	4.211	2.354	2.3533	0.03		
Mole Fraction	0.07128				2.3564	0.10
Normality	6.305	4.062	4.0742	0.30		
Mole Fraction	0.10478				4.0791	0.42
Normality	8.379	7.064	7.0436	0.28		
Mole Fraction	0.13745				7.0360	0.40
Normality	10.366	11.631	11.6259	0.04		
Mole Fraction	0.16874				11.6102	0.17
Normality	12.250	17.872	17.8818	0.05		
Mole Fraction	0.19871				17.9065	0.19

[a] Equation for normality: $\eta = \eta_0 \exp(AN + BN^2 + CN^3)$ $\eta_0 = 0.8913$ $A = 0.19518994$ $B = 0.01068781$ $C = -0.00054187$

[b] Equation for mole fraction: $\eta = \eta_0 \exp(AX + BX^2 + CX^3)$ $\eta_0 = 0.8913$ $A = 10.6039950$ $B = 53.75068270$ $C = -156.6708017$

Table 12. Calculated Viscosities of the 2:1 Mixture Solutions at 25.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.8913	0.89130	0.00		
Mole Fraction	0.00000				0.89130	0.00
Normality	2.163	1.320	1.3211	0.10		
Mole Fraction	0.03781				1.3208	0.16
Normality	4.344	2.058	2.0549	0.17		
Mole Fraction	0.07439				2.0551	0.16
Normality	6.497	3.272	3.2715	0.01		
Mole Fraction	0.10988				3.2721	0.01
Normality	8.574	5.184	5.1863	0.06		
Mole Fraction	0.14396				5.1860	0.04
Normality	10.602	8.1158	8.1236	0.09		
Mole Fraction	0.17752				8.1228	0.08
Normality	12.563	12.370	12.3603	0.08		
Mole Fraction	0.21057				12.3614	0.07

[a]Equation for normality: $\eta = \eta_o \exp (AN + BN^2 + CN^3)$ $\eta_o = 0.8913$ A = 0.16915972

B = 0.00644916 C = -0.00025894

[b]Equation for mole fraction: $\eta = \eta_o \exp (AX + BX^2 + CX^3)$ $\eta_o = 0.8913$

A = 9.32456671 B = 31.39774438 C = -77.7526449

Table 13. Calculated Viscosities of the 1:1 Mixture Solutions at 25.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.8913	0.89130	0.00		
Mole Fraction	0.00000				0.89130	0.00
Normality	2.214	1.283	1.2842	0.10		
Mole Fraction	0.03883				1.2842	0.09
Normality	4.414	1.921	1.9186	0.10		
Mole Fraction	0.07609				1.9184	0.11
Normality	6.598	2.943	2.9409	0.06		
Mole Fraction	0.11265				2.9408	0.06
Normality	8.674	4.499	4.4932	0.12		
Mole Fraction	0.14748				4.4937	0.11
Normality	10.724	6.864	6.8907	0.38		
Mole Fraction	0.18228				6.8906	0.38
Normality	12.725	10.492	10.4719	0.19		
Mole Fraction	0.21708				10.4718	0.19

[a]Equation for normality: $\eta = \eta_o \exp (AN + BN^2 + CN^3)$ $\eta_o = 0.8913$ A = 0.15467190

B = 0.00496879 C = -0.00015000

[b]Equation for mole fraction: $\eta = \eta_o \exp (AX + BX^2 + CX^3)$ $\eta_o = 0.8913$ A = 8.55816277

B = 23.74775712 C = -50.1614050

Table 14. Calculated Viscosities of the 1:2 Mixture Solutions at 25.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.8913	0.89130	0.00		
Mole Fraction	0.00000				0.89130	0.00
Normality	2.268	1.237	1.2418	0.43		
Mole Fraction	0.03990				1.2421	0.45
Normality	4.486	1.795	1.7808	0.75		
Mole Fraction	0.07785				1.7806	0.79
Normality	6.702	2.637	2.6334	0.13		
Mole Fraction	0.11557				2.6336	0.13
Normality	8.777	3.873	3.8941	0.55		
Mole Fraction	0.15118				3.8950	0.58
Normality	10.849	5.865	5.8734	0.17		
Mole Fraction	0.18732				5.8727	0.14
Normality	12.892	8.977	8.9542	0.26		
Mole Fraction	0.22401				8.9553	0.25

[a]Equation for normality: $\eta = \eta_o \exp(AN + BN^2 + CN^3)$ $\eta_o = 0.8913$ A = 0.13741001

B = 0.00404178 C = -0.000063488

[b]Equation for mole fraction: $\eta = \eta_o \exp(AX + BX^2 + CX^3)$ $\eta_o = 0.8913$ A = 7.62292174

B = 18.57391522 C = -29.5674506

Table 15. Calculated Viscosities of the Potassium Hydroxide Solutions at 25.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Cal.[b] (cp)	% Error
Normality	0.000	0.8913	0.89130	0.00		
Mole Fraction	0.00000				0.89130	0.00
Normality	2.383	1.164	1.1655	0.13		
Mole Fraction	0.04223				1.1651	0.09
Normality	4.638	1.548	1.5442	0.23		
Mole Fraction	0.08166				1.5443	0.23
Normality	6.920	2.127	2.1290	0.06		
Mole Fraction	0.12192				2.1302	0.14
Normality	8.991	2.961	2.9641	0.12		
Mole Fraction	0.15921				2.9640	0.11
Normality	11.108	4.352	4.3541	0.06		
Mole Fraction	0.19838				4.3465	0.12
Normality	13.239	6.770	6.7696	0.01		
Mole Fraction	0.23951				6.7719	0.02

[a]Equation for normality: $\eta = \eta_o \exp(AN + BN^2 + CN^3)$ $\eta_o = 0.8913$ A = 0.10770164

B = 0.00173065 C = 0.00012859

[b]Equation for mole fraction: $\eta = \eta_o \exp(AX + BX^2 + CX^3)$ $\eta_o = 0.8913$ A = 5.94571944

B = 9.14333027 C = 5.7712177

Table 16. Calculated Viscosities of the Sodium Hydroxide Solutions at 35.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.7203	0.72030	0.00		
Mole Fraction	0.00000				0.72030	0.00
Normality	2.068	1.116	1.1138	0.20		
Mole Fraction	0.03597				1.1132	0.25
Normality	4.211	1.823	1.8282	0.28		
Mole Fraction	0.07128				1.8297	0.37
Normality	6.305	3.017	3.0231	0.20		
Mole Fraction	0.10478				3.0252	0.27
Normality	8.379	4.959	4.9439	0.30		
Mole Fraction	0.13745				4.9396	0.39
Normality	10.366	7.714	7.7016	0.16		
Mole Fraction	0.16874				7.6950	0.25
Normality	12.250	11.195	11.2148	0.18		
Mole Fraction	0.19871				11.2231	0.25

[a] Equation for normality: $\eta = \eta_o \exp (AN + BN^2 + CN^3)$ $\eta_o = 0.7203$ A = 0.19678564

B = 0.00767084 C = -0.00044414

[b] Equation for mole fraction: $\eta = \eta_o \exp (AX + BX^2 + CX^3)$ $\eta_o = 0.7203$ A = 10.76150808

B = 42.08773874 C = -134.3614461

Table 17. Calculated Viscosities of the Sodium Hydroxide Solutions at 45.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.5970	0.59700	0.00		
Mole Fraction	0.00000				0.59700	0.00
Normality	2.068	0.9191	0.91745	0.18		
Mole Fraction	0.03597				0.91722	0.20
Normality	4.211	1.466	1.4689	0.19		
Mole Fraction	0.07128				1.4695	0.24
Normality	6.305	2.331	2.3398	0.40		
Mole Fraction	0.10478				2.3406	0.41
Normality	8.379	3.678	3.6599	0.48		
Mole Fraction	0.13745				3.6578	0.55
Normality	10.366	5.455	5.4507	0.08		
Mole Fraction	0.16874				5.4490	0.01
Normality	12.250	7.608	7.6208	0.16		
Mole Fraction	0.19871				7.6234	0.20

[a]Equation for normality: $\eta = \eta_o \exp(AN + BN^2 + CN^3)$ $\eta_o = 0.5970$ A = 0.19886924

B = 0.00502536 C = -0.00035010

[b]Equation for mole fraction: $\eta = \eta_o \exp(AX + BX^2 + CX^3)$ $\eta_o = 0.5970$ A = 10.93721619

B = 31.88866464 C = -112.8474545

Table 18. Calculated Viscosities of the Sodium Hydroxide Solutions at 55.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.5049	0.50490	0.000		
Mole Fraction	0.00000				0.50490	0.00
Normality	2.068	0.7711	0.76964	0.19		
Mole Fraction	0.03597				0.76963	0.19
Normality	4.211	1.203	1.2045	0.16		
Mole Fraction	0.07128				1.2047	0.14
Normality	6.305	1.851	1.8587	0.44		
Mole Fraction	0.10478				1.8588	0.42
Normality	8.379	2.813	2.8032	0.34		
Mole Fraction	0.13745				2.8023	0.38
Normality	10.366	4.043	4.0290	0.35		
Mole Fraction	0.16874				4.0295	0.33
Normality	12.250	5.447	5.4625	0.28		
Mole Fraction	0.19871				5.4627	0.29

[a] Equation for normality: $\eta = \eta_o \exp (AN + BN^2 + CN^3)$ $\eta_o = 0.5049$ A = 0.19894467

B = 0.00292942 C = -0.00026948

[b] Equation for mole fraction: $\eta = \eta_o \exp (AX + BX^2 + CX^3)$ $\eta_o = 0.5049$ A = 10.98926870

B = 23.68947121 C = -94.0228257

Table 19. Calculated Viscosities of the Sodium Hydroxide Solutions at 65.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality Mole Fraction	0.000 0.00000	0.4346	0.43460	0.00	0.43460	0.00
Normality Mole Fraction	2.068 0.03597	0.6602	0.65863	0.23	0.65876	0.22
Normality Mole Fraction	4.211 0.07128	1.008	1.0115	0.37	1.0114	0.34
Normality Mole Fraction	6.305 0.10478	1.516	1.5189	0.17	1.5186	0.17
Normality Mole Fraction	8.379 0.13745	2.227	2.2187	0.39	2.2184	0.39
Normality Mole Fraction	10.366 0.16874	3.091	3.0887	0.06	3.0901	0.03
Normality Mole Fraction	12.250 0.19871	4.064	4.0696	0.15	4.0686	0.11

[a] Equation for normality: $\eta = \eta_0 \exp (AN + BN^2 + CN^3)$ $\eta_0 = 0.4346$ A = 0.19963049

B = 0.00109213 C = -0.00020265

[b] Equation for mole fraction: $\eta = \eta_0 \exp (AX + BX^2 + CX^3)$ $\eta_0 = 0.4346$ A = 11.06935957

B = 16.54923057 C = -78.5626198

Table 20. Calculated Viscosities of the Sodium Hydroxide Solutions at 75.0°C

	Concentration	Viscos. Exp. (cp)	Viscos. Calc.[a] (cp)	% Error	Viscos. Calc.[b] (cp)	% Error
Normality	0.000	0.3791	0.37910	0.00		
Mole Fraction	0.00000				0.37910	0.00
Normality	2.068	0.5735	0.57216	0.24		
Mole Fraction	0.03597				0.57239	0.19
Normality	4.211	0.8617	0.86485	0.36		
Mole Fraction	0.07128				0.86451	0.33
Normality	6.305	1.265	1.2687	0.25		
Mole Fraction	0.10478				1.2682	0.25
Normality	8.379	1.812	1.8036	0.46		
Mole Fraction	0.13745				1.8037	0.46
Normality	10.366	2.447	2.4452	0.08		
Mole Fraction	0.16874				2.4472	0.01
Normality	12.250	3.144	3.1492	0.17		
Mole Fraction	0.19871				3.1477	0.12

[a] Equation for normality: $\eta = \eta_o \exp (AN + BN^2 + CN^3)$ $\eta_o = 0.3791$ A = 0.20081083

B = -0.00059844 C = -0.00013771

[b] Equation for mole fraction: $\eta = \eta_o \exp (AX + BX^2 + CX^3)$ $\eta_o = 0.3791$ A = 11.17371399

B = 9.99904185 C = -63.5486025

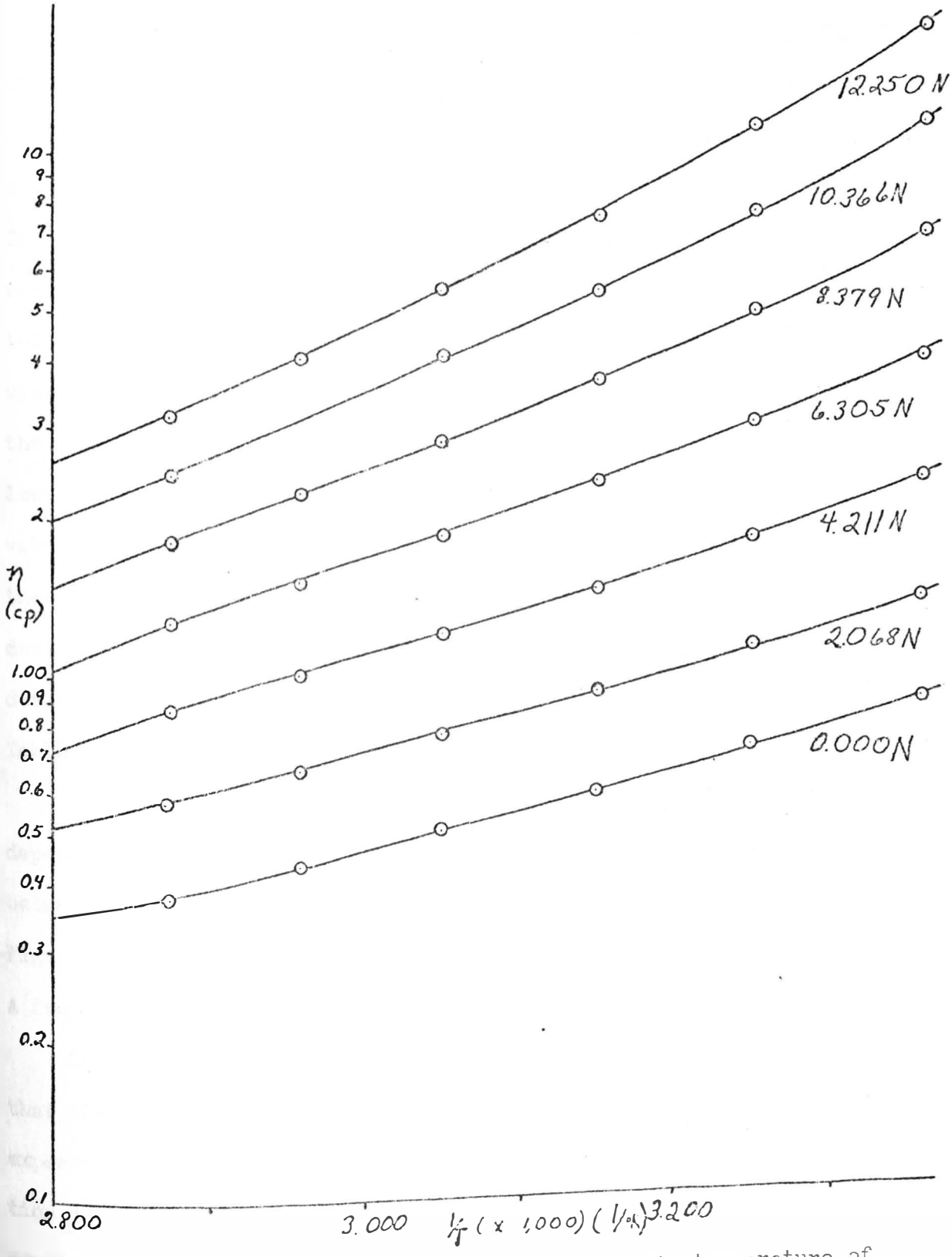


Figure 12. Relation of log η and inverse absolute temperature of NaOH solutions for various concentrations

calculations. The method used by C. T. Moynihan was employed. The quantity $(T - T_o)$ was treated as the variable, T, for selected values of T_o. The constants A and B were solved for in the usual least squares method. An IBM 360 computer was used to do the calculations. The initial T_o value was increased by a specified interval over a set range, and the constants A and B were obtained for each T_o value over that range. The absolute value of the percent deviation for each viscosity point was calculated and summed for each set of values for the empirical constants. The set of empirical constants which gave the lowest summed percent deviations was then chosen as the best set of values. The empirical constants, A, B, and T_c, for the best set were then printed out along with the calculated viscosity and their percent deviations. The accuracy was within experimental error; the average deviation never exceeding 0.2% error. The results are presented in Table 21.

An attempt was made to combine the concentration and temperature dependent viscosity equations into one equation, but a relationship between the constants of the two equations had to be found first. As Figure 13 shows, the temperature dependence of the empirical constant A from the concentration dependent equation is very scattered.

Looking at the problem from the other direction, Figure 14 shows that the concentration dependence of T_o is almost linear, within experimental error. But as Figures 15, 16, and 17 show, the concentration dependence of the other two empirical constants in the temperature dependent equation are not linear, and shows much scatter. Since a

Table 21. Temperature Dependent Equations for the Viscosity of the Sodium Hydroxide Solutions for Various Concentrations[a]

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C	75.0°C
2.068	Viscos. Exp.[b]	1.391	1.116	0.9191	0.7711	0.6602	0.5736
	Viscos. Calc.[b]	1.3909	1.1164	0.91857	0.77172	0.66000	0.57357
	% Error	0.008	0.040	0.058	0.080	0.022	0.004
4.211	Viscos. Exp.[c]	2.354	1.823	1.466	1.203	1.008	0.8617
	Viscos. Calc.[c]	2.3520	1.8278	1.4637	1.2020	1.0083	0.86183
	% Error	0.087	0.262	0.163	0.051	0.045	0.010
6.305	Viscos. Exp.[d]	4.062	3.017	2.331	1.851	1.516	1.265
	Viscos. Calc.[d]	4.0620	3.0176	2.3283	1.8534	1.5144	1.2660
	% Error	0.001	0.021	0.100	0.157	0.128	0.040
8.379	Viscos. Exp.[e]	7.064	4.959	3.678	2.813	2.228	1.812
	Viscos. Calc.[e]	7.0610	4.9700	3.6677	2.8130	2.2274	1.8130
	% Error	0.043	0.221	0.270	0.008	0.001	0.055
10.366	Viscos. Exp.[f]	11.631	7.714	5.455	4.043	3.091	2.447
	Viscos. Calc.[f]	11.6186	7.7358	5.4552	4.0295	3.0914	2.4500
	% Error	0.106	0.282	0.003	0.337	0.023	0.119
12.250	Viscos. Exp.[g]	17.872	11.195	7.608	5.447	4.064	3.144
	Viscos. Calc.[g]	17.8203	11.2497	7.6084	5.4356	4.0590	3.1469
	% Error	0.289	0.489	0.003	0.215	0.112	0.093

[a] Equation for degrees Kelvin: $\eta = AT^{1/2}\exp(B/(T - T_o))$ or $\ln \eta = \ln A + 1/2 \ln T + B/(T - T_o)$

[b] T_o = 130.8	A = 0.0012194000	lnA = -6.7093964	B = 701.28882
[c] T_o = 142.3	A = 0.0015820849	lnA = -6.4490118	B = 694.38281
[d] T_o = 154.7	A = 0.0019094399	lnA = -6.2609453	B = 690.54590
[e] T_o = 164.4	A = 0.0020718237	lnA = -6.1793261	B = 706.88477
[f] T_o = 172.2	A = 0.0021328987	lnA = -6.1502733	B = 724.72876
[g] T_o = 180.9	A = 0.0024011901	lnA = -6.0317907	B = 710.92749

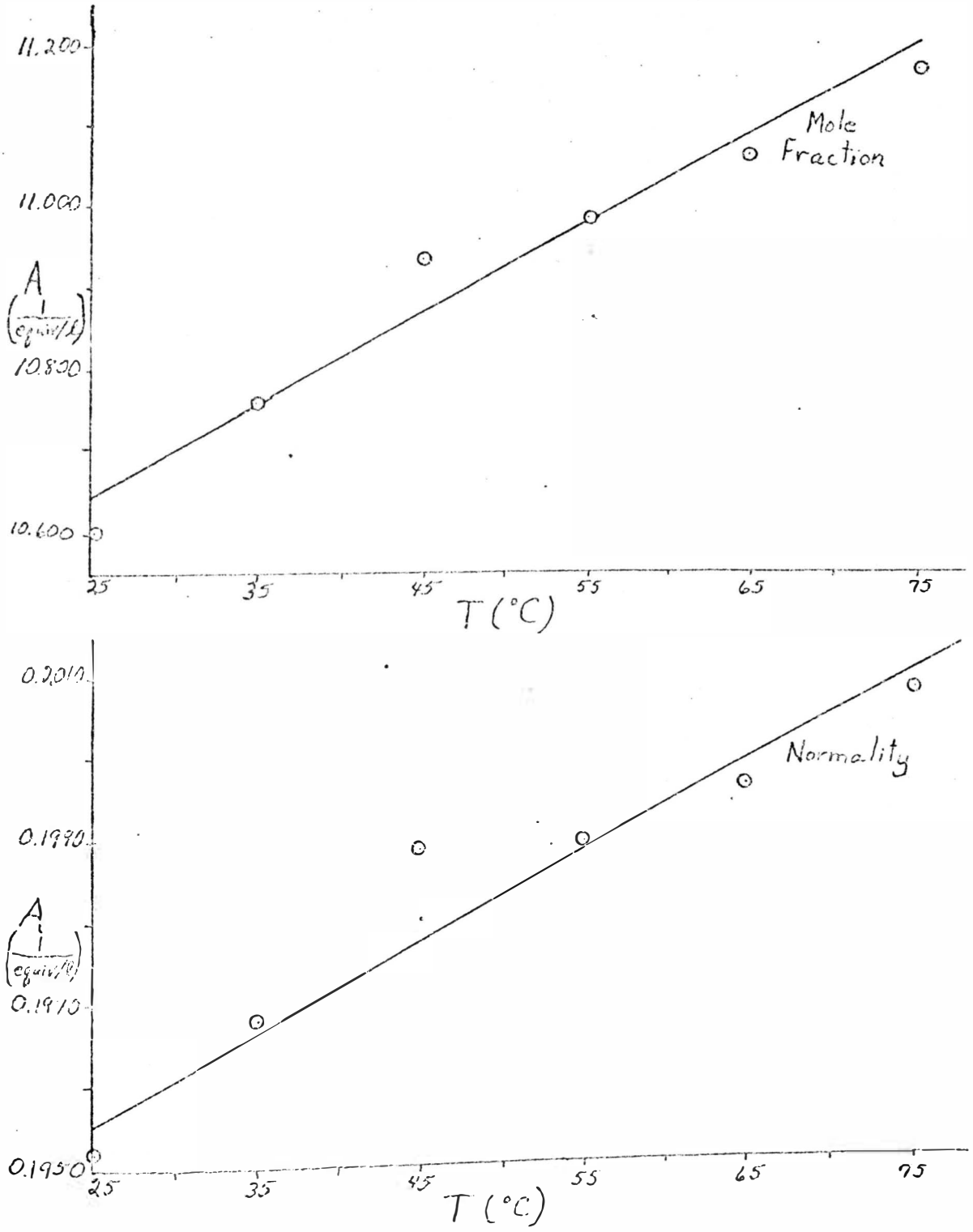


Figure 13. Relation of A and temperature from the concentration dependent equations of viscosity of the aqueous NaOH solutions

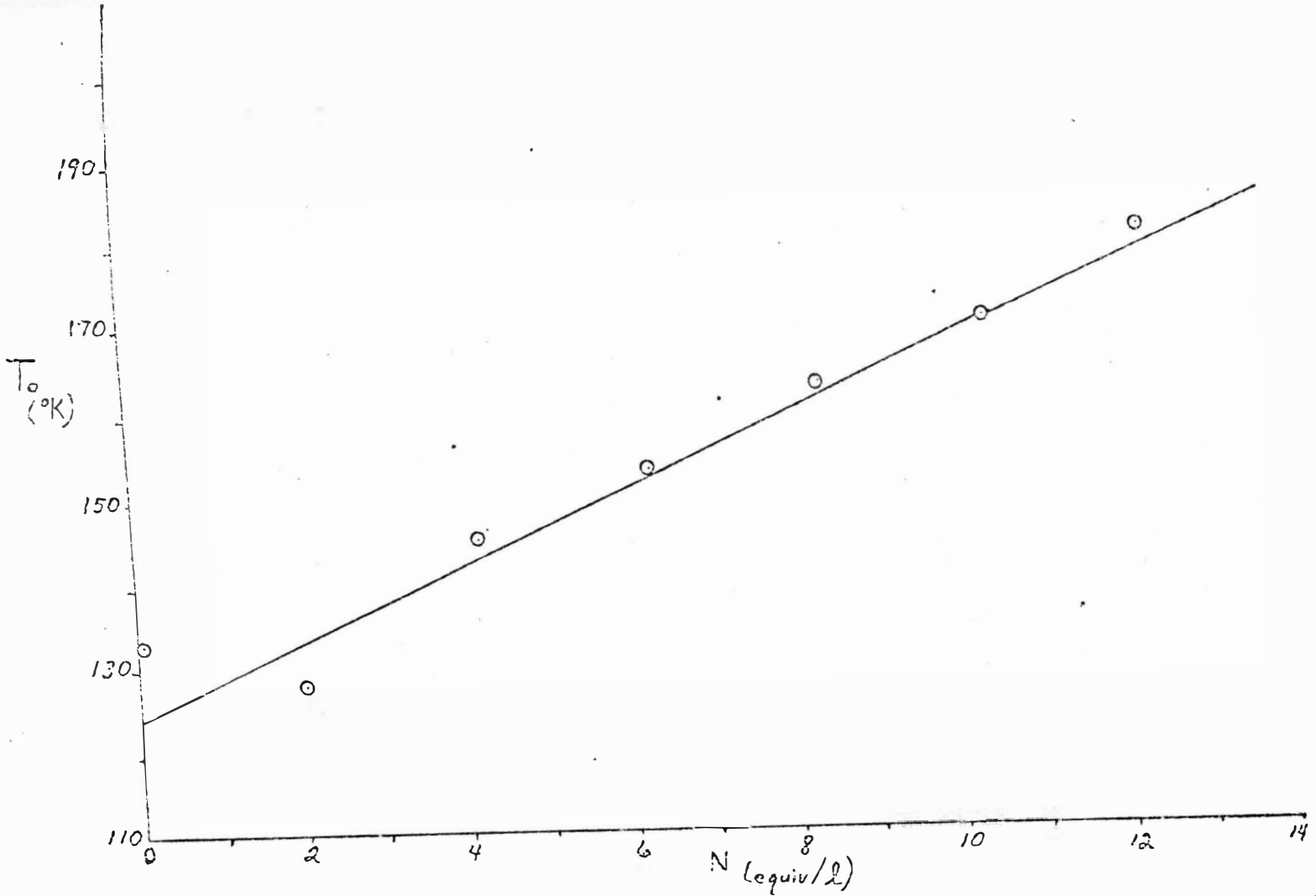


Figure 14. Relation of T_o and concentration for the temperature dependent equations of viscosity of the aqueous NaOH solutions

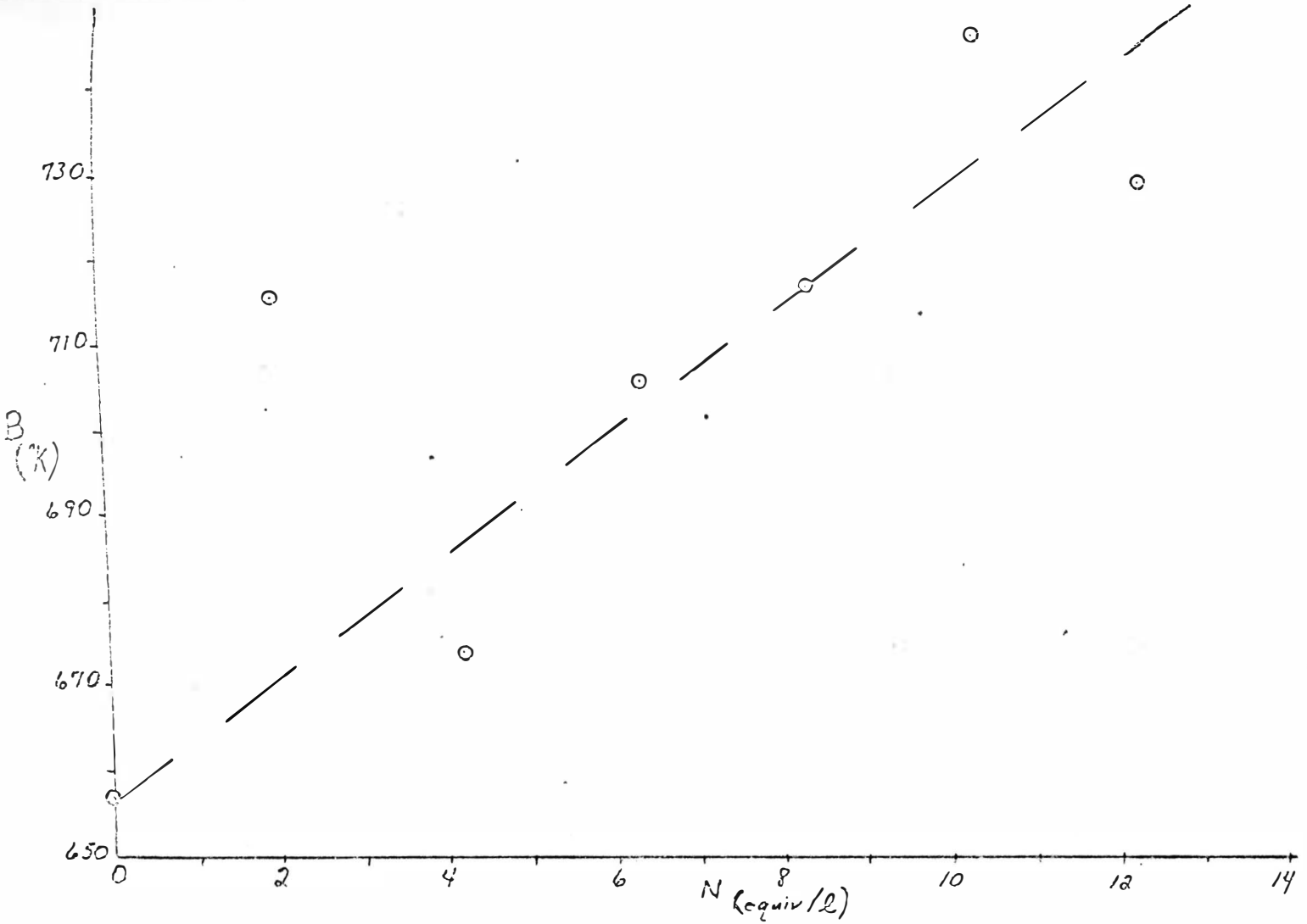


Figure 15. Relation of B and concentration of the temperature dependent equations of viscosity of the aqueous NaOH solutions

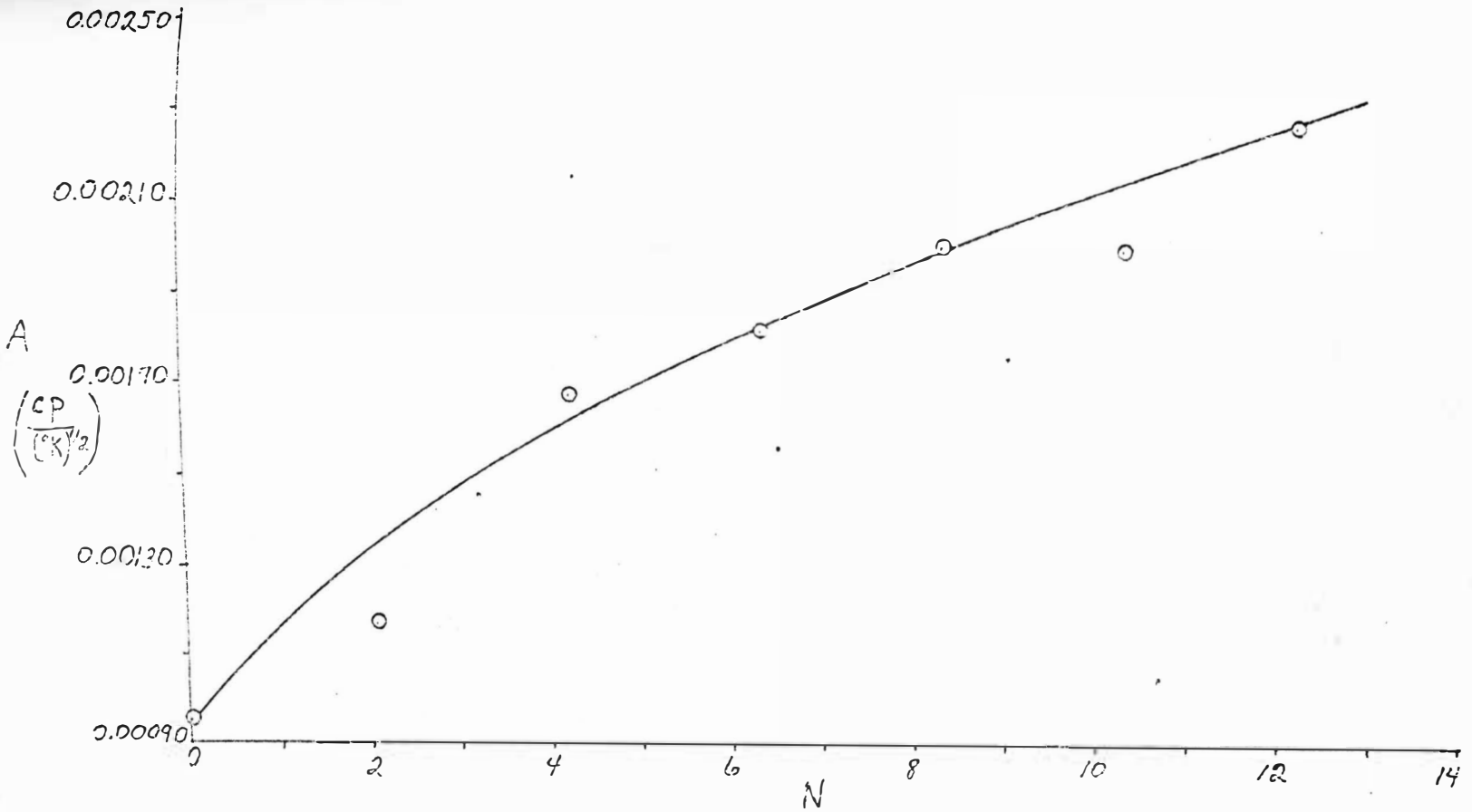


Figure 16. Relation of A and concentration of the temperature dependent equations of the viscosity of the aqueous NaOH solutions

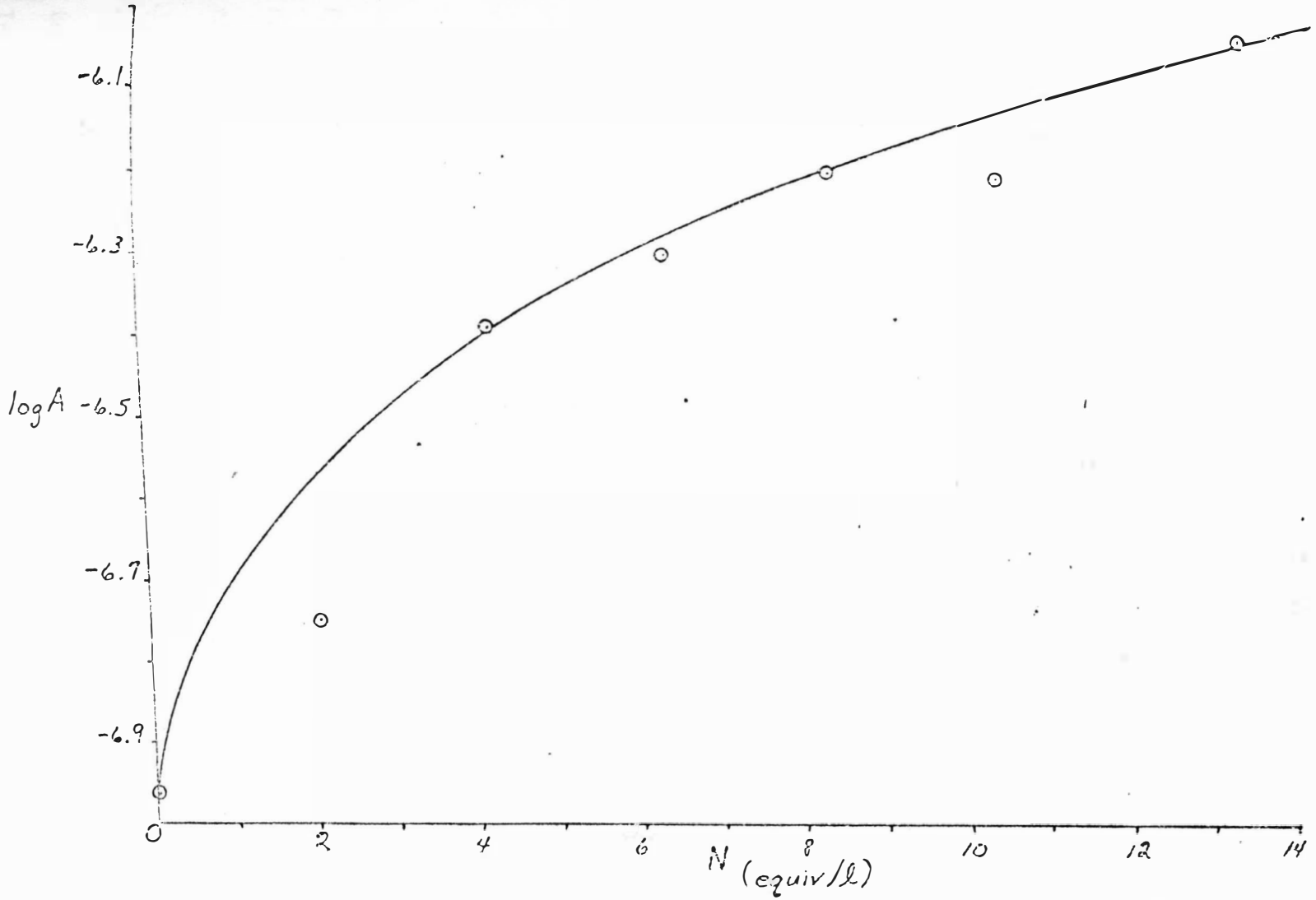


Figure 17. Relation of log A and concentration of the temperature dependent equations of the viscosity of the aqueous NaOH solutions

simple solution was being sought for sake of utility, no further work was done with these equations.

The equivalent conductance values of A. Woo (8) were fitted to the temperature dependent equations used by C. A. Angell (36,41) and C. T. Moynihan (39). The results for the NaOH solutions are presented in Table 22, and for the KOH solutions in Table 23. The equations for the temperature dependence of the equivalent conductance is

$$\Lambda = AT^{\frac{1}{2}}\exp(-B/(T - T_o))$$

where T_o, A, and B are empirical constants which were solved for in the same manner as they were for the temperature dependent equation for the viscosity of the NaOH solutions.

Due to an error in choosing the limits for T_o, the first two data points in the NaOH solutions values are high. A couple of limits were chosen wrong for the KOH solutions, but the error involved was much less. The percent error in the calculated results was much higher for the equivalent conductance equations than for the viscosity equations. In some instances it was as high as 1%. As can be seen from Figure 18, the T_o values do not form a continuous line as they did for the viscosity values when T_o is plotted against the concentration of the solution.

In attempts to extend the limiting law infinite dilution conductance equations to regions of higher concentration, it became necessary to include the viscosity of the solution in the conductance equation. In the limiting law case it was felt that the viscosity of the solution

Table 22. Temperature Dependent Equations for the Equivalent Conductance of the Sodium Hydroxide Solutions of A. Woo for Various Concentrations[a]

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C
2.332	eq. cond. exp.[b]	141.5	161.5	183.2	236.2	267.3
	eq. cond. calc.	136.91	164.395	194.831	228.201	264.464
	% error	3.24	1.79	6.35	3.39	1.06
2.799	eq. cond. exp.[c]	130.7	146.8	170.8	213.3	239.0
	eq. cond. calc.	126.71	150.97	177.63	206.65	237.98
	% error	3.05	2.84	4.00	3.11	0.42
3.359	eq. cond. exp.[d]	115.7	140.6	165.6	194.1	224.4
	eq. cond. calc.	115.96	139.83	165.92	194.11	224.26
	% error	0.23	0.55	0.20	0.01	0.06
4.031	eq. cond. exp.[e]	100.4	122.1	147.1	173.7	202.9
	eq. cond. calc.	100.38	122.33	146.77	173.70	203.04
	% error	0.02	0.19	0.22	0.00	0.07
4.837	eq. cond. exp.[f]	85.00	104.8	125.9	152.3	177.9
	eq. cond. calc.	85.002	104.81	126.99	151.51	178.29
	% error	0.00	0.01	0.87	0.52	0.22
5.804	eq. cond. exp.[g]	68.31	86.58	104.2	126.9	150.5
	eq. cond. calc.	68.388	85.932	104.81	126.99	150.06
	% error	0.11	0.75	1.22	0.01	0.29
6.965	eq. cond. exp.[h]	52.17	68.92	84.97	103.4	125.4
	eq. cond. calc.	52.604	67.806	85.026	104.15	125.04
	% error	0.83	1.62	0.07	0.73	0.29

Table 22. Continued

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C
8.358	eq. cond. exp.[i]	37.87	50.77	66.25	83.27	102.2
	eq. cond. calc.[i]	37.864	50.905	66.067	82.256	102.34
	% error	0.01	0.27	0.27	0.02	0.14
10.03	eq. cond. exp.[j]	26.38	35.80	49.77	63.54	79.84
	eq. cond. calc.[j]	26.121	36.589	49.086	63.550	79.872
	% error	0.98	2.20	1.37	0.02	0.04
12.04	eq. cond. exp.[k]	18.01	25.33	35.54	48.07	60.62
	eq. cond. calc.[k]	17.863	25.748	35.540	47.312	61.086
	% error	0.82	1.65	0.00	1.23	0.74

[a]Equation for degrees Kelvin: $\Lambda = AT^{-1/2}\exp(-B/(T - T_o))$ or $\ln\Lambda = \ln A - 1/2\ln T - B/(T - T_o)$

[b]T_o = 25.0	A = 670105.69	lnA = 13.415191	B = 1542.4958
[c]T_o = 25.0	A = 497746.63	lnA = 13.117846	B = 1482.4194
[d]T_o = 73.2	A = 239796.88	lnA = 12.387547	B = 1076.4954
[e]T_o = 50.8	A = 429394.31	lnA = 12.970131	B = 1363.4768
[f]T_o = 67.8	A = 335482.38	lnA = 12.723325	B = 1251.2292
[g]T_o =113.2	A = 139697.13	lnA = 11.847232	B = 882.8091
[h]T_o =125.6	A = 126369.25	lnA = 11.746964	B = 851.5996
[i]T_o =143.4	A = 112443.19	lnA = 11.630203	B = 796.5603
[j]T_o =156.4	A = 96384.06	lnA = 11.476096	B = 760.4297
[k]T_c =143.8	A = 164632.94	lnA = 12.011474	B = 969.3105

Table 23. Temperature Dependent Equations for the Equivalent Conductance of the Potassium Hydroxide Solutions of A. Woo for Various Concentrations[a]

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C
2.299	eq. cond. exp.[b]	180.8	215.9	246.8	275.8	313.2
	eq. cond. calc.	181.38	214.07	246.80	279.18	310.90
	% error	0.32	0.84	0.00	1.23	0.73
2.758	eq. cond. exp.[c]	171.3	201.2	232.7	260.3	294.1
	eq. cond. calc.	171.29	201.18	231.64	262.31	292.92
	% error	0.01	0.01	0.46	0.77	0.40
3.310	eq. cond. exp.[d]	159.7	187.2	213.9	243.1	276.2
	eq. cond. calc.	159.70	186.66	214.99	244.47	274.90
	% error	0.00	0.39	0.51	0.57	0.47
3.972	eq. cond. exp.[e]	143.0	171.4	197.4	221.4	255.9
	eq. cond. calc.	143.27	169.98	197.38	225.16	253.02
	% error	0.19	0.82	0.01	1.70	1.13
4.766	eq. cond. exp.[f]	127.2	152.6	176.8	200.0	232.6
	eq. cond. calc.	127.11	151.88	177.44	203.44	229.61
	% error	0.07	0.47	0.36	1.72	1.28
5.719	eq. cond. exp.[g]	108.9	133.8	154.0	176.5	205.7
	eq. cond. calc.	109.99	131.1	154.01	178.53	204.54
	% error	1.00	1.99	0.01	1.15	0.56
6.863	eq. cond. exp.[h]	91.75	112.3	131.9	154.5	176.9
	eq. cond. calc.	91.93	111.78	132.72	154.48	176.83
	% error	0.20	0.46	0.62	0.01	0.03

Table 23. Continued

Normality		25.0°C	35.0°C	45.0°C	55.0°C	65.0°C
8.236	eq. cond. exp. [i]	73.19	90.57	109.1	128.7	147.4
	eq. cond. calc.	73.170	90.647	109.086	128.200	147.735
	% error	0.03	0.08	0.01	0.39	0.23
9.883	eq. cond. exp. [j]	55.90	70.12	85.02	101.4	118.3
	eq. cond. calc.	55.925	70.029	85.259	101.41	118.27
	% error	0.04	0.12	0.28	0.01	0.02
11.86	eq. cond. exp. [k]	39.28	50.64	62.58	73.24	90.02
	eq. cond. calc.	39.276	50.386	62.424	75.184	88.474
	% error	0.01	0.50	0.24	2.64	1.71

[a] Equation for degrees Kelvin: $\Lambda = AT^{-1/2}\exp(-B/(T - T_o))$ or $\ln\Lambda = \ln A - 1/2\ln T - b/(T - T_o)$

$^{b}T_o = 166.0$	A = 41749.406	lnA = 10.639441	B = 342.27417
$^{c}T_o = 144.5$	A = 53874.320	lnA = 10.894409	B = 445.93018
$^{d}T_o = 91.6$	A = 115574.63	lnA = 11.657672	B = 771.58496
$^{e}T_o = 147.6$	A = 50141.781	lnA = 10.822610	B = 453.01465
$^{f}T_o = 150.0$	A = 47646.594	lnA = 10.771566	B = 455.96924
$^{g}T_o = 69.0$	A = 188535.63	lnA = 12.147043	B = 1053.5977
$^{h}T_o = 143.6$	A = 51928.504	lnA = 10.857623	B = 539.03467
$^{i}T_o = 162.0$	A = 36791.371	lnA = 10.513019	B = 459.02148
$^{j}T_o = 149.0$	A = 44354.070	lnA = 10.699960	B = 568.52124
$^{k}T_o = 168.0$	A = 28046.527	lnA = 10.241620	B = 484.44556

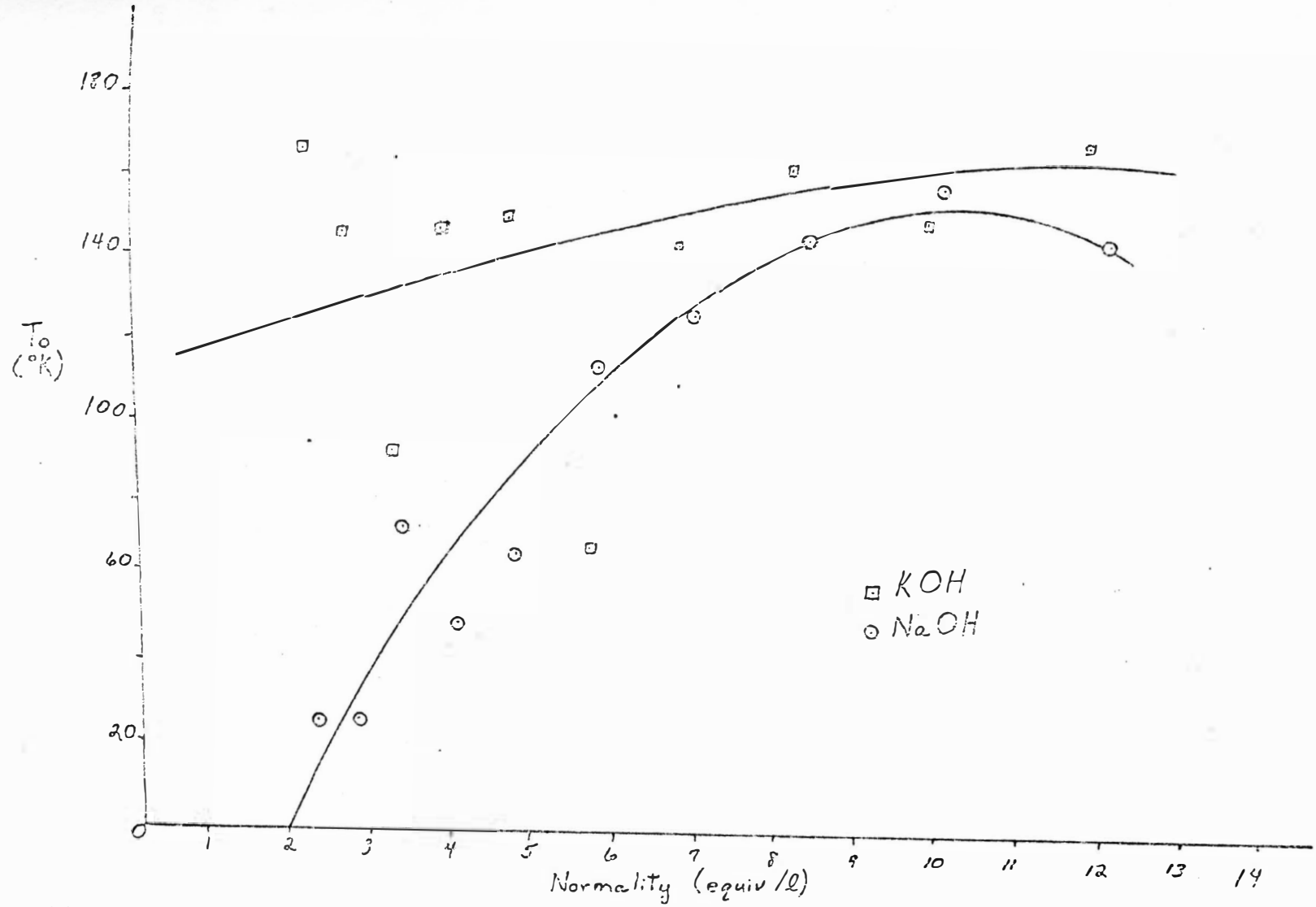


Figure 18. Relation of T_o and concentration of the temperature dependent equations of the equivalent conductance of the aqueous NaOH and KOH solutions of A. Woo

and the viscosity of the solvent were similar, such that the terms would be close to unity.

A. Woo (8) used the Robinson-Stokes equation of equivalent conductance for his NaOH, KOH, and mixture solutions. His calculated equivalent conductances were high compared to his measured values. For the NaOH solutions at 25.0°C he multiplied the calculated values by the viscosity correction, η/η_0, and was able to obtain a close fit between the experimental values and the calculated values. However, the values for the viscosity of the NaOH solutions at 25.0°C that he used were in error. This was one reason for pursuing this project.

The conductance equation proposed by B. F. Wishaw and R. H. Stokes (11) for the equivalent conductance of electrolytic solutions has had some success. At the time this equation was considered semi-empirical, because the viscosity correction was qualitatively introduced to explain the effect of viscosity on the conductance. Other workers such as A. N. Campbell (12,13) have used similar approaches.

The inclusion of the viscosity term can be easily shown. The basic force equation for electrical conductance proposed by Debye, Huckel, and Onsager can be expressed in terms of mobility in electrostatic units as:

$$\mu_i = \frac{\lambda_i}{F} = \frac{eZ_i}{300f_i} - \frac{eK}{300}\left[\frac{Z_i}{6\pi\eta} + \frac{e^2 Z_i W}{6DkTf_i}\right]$$

where μ_i = mobility of the individual ion, i

λ_i = equivalent conductivity on the i^{th} ion

f_i = electric force on i^{th} ion

F = Faraday's constant

eZ_i = charge on the i^{th} ion

η = viscosity of the solution

D = dielectric constant of the solution

k = Boltzmann constant

T = absolute temperature

$W = Z_+ Z_- (2q/(1+q))$ $q = \frac{1}{2}$ for symmetrical electrolytes

$$K^2 = \frac{4\pi e^2}{DkT} \sum_i N_i Z_i^2 = \frac{8\pi N_o^2 e^2 d_o I}{1000\ DRT}$$

I = ionic charge $= \frac{1}{2} \sum_i m_i Z_i^2$

N_o = Avogadro's number

d_o = density of the solvent

R = gas law constant

Since $K \rightarrow 0$ as the concentration approaches zero, it is normally assumed that $eZ_i/300f_i = \mu_i^o$ = mobility at infinite dilution. One must consider; however, that where $f_i \longrightarrow f_i^o$, $f_i \neq f_i^o$ for all concentrations.

One can now suggest that the following relationship must be used:

$$\frac{\lambda_i^o}{F} = \mu_i^o = \frac{eZ_i}{300f_i^o} = \frac{eZ_i(f_i)}{300f_i(f_i^o)}$$

This is necessary to account for the fact that $f_i \neq f_i^o$ at all concentrations. Assuming that f_i can be described by Stokes' force law, $f_i = \left[6\pi\eta r_i\right] v_i$, the expression for mobility can be changed to account for the change in f_i with concentration. At infinite dilution

Force = $eZ_i x = (6\pi\eta r_i)\, v_i$ and $f_i / f_i^{o} = \eta r_i / \eta_o r_i^{o}$ where

r_i^{o} = radius of hydrated i^{th} ion at infinite dilution

r_i = radius of the i^{th} ion

η = viscosity of the solution

η_o = viscosity of the solvent.

The expression for mobility now becomes

$$\mu_i = \frac{\lambda_i}{F} = \frac{\lambda_i^{o}\,\eta_o r_i^{o}}{F\,\eta r_i} - \frac{eK}{300}\left[\frac{Z_i}{6\pi\eta} + \frac{e^2 Z_i W}{6Dk\,Tf_i}\right]$$

The $(\eta_o r_i^{o}/\eta r_i)$ term is usually left out of most derivations, because in the case of infinite dilution studies the viscosity of the solution is very similar to the viscosity of the solvent.

The mobility expression can now be rewritten as

$$\lambda_i = \lambda_i^{o}\left[\frac{\eta_o r_i^{o}}{\eta r_i}\right] - \frac{eKFZ_i}{300(6\pi\eta)} - \frac{e^2 KW}{6DkT}\lambda_i^{o}\left[\frac{\eta_o r_i^{o}}{\eta r_i}\right]$$

To obtain the conductance equation in its final form, the condition, $r_i = r_i^{o}$, must be involved. In terms of physical meaning, this implies that the radius of the hydrated ions is constant for all concentrations.

One is left with the final expression:

$$\lambda_i = \frac{\eta_o}{\eta}\left[\lambda_i^{o} - \frac{e^2 KW}{6kDT}\lambda_i^{o} - \frac{eKFZ_i}{(300)6\pi\eta_o}\right]$$

This is basically the Onsager equation for electrical conductance, but including the correction for the change of viscosity of the solution with concentration.

B. F. Wishaw and R. H. Stokes (11) have treated the conductance of concentrated solutions in a similar manner. The equation they have proposed has been successful in many cases up to concentrations of 5 - 6 molar (11, 12, 13). The Wishaw-Stokes equation was applied to the NaOH solutions measured at 25.0°C used in this work. The purpose of this short derivation of the Onsager equation has been to show the basic assumptions that are needed in making viscosity corrections to conductance equations.

The Wishaw-Stokes conductance equation can be written as:

$$\Lambda = \left[\Lambda_o - \frac{B_2 c^{\frac{1}{2}}}{1 + Ba^o c^{\frac{1}{2}}}\right]\left[1 - \frac{B_1 c^{\frac{1}{2}} F}{1 + Ba^o c^{\frac{1}{2}}} \frac{\eta_o}{\eta}\right]$$

where Λ = equivalent conductance at concentration, c

Λ_o = equivalent conductance at infinite dilution

$B_1 = 8.20 \times 10^5/(D_o T)^{3/2}$

D_o = dielectric constant of the solvent

$B_2 = 82.5/\ _o(D_o T)^{\frac{1}{2}}$

$B = 50.29/\ (D_o T)^{\frac{1}{2}}$

η_o = viscosity of the solvent

η = viscosity of the solution

a^o = mean distance of closest approach of ions ($\mathring{A}$)

$$F = \frac{(e^{0.2929Ka^o} - 1)}{0.2929Ka^o}$$

K = Debye-Huckel constant defined by

$$K^2 = \frac{4\ Ne^2}{1000\ DkT}\ C(v_1 z_1^2 + v_2 z_2^2)$$

The results obtained by using my viscosity data for NaOH solutions at 25.0°C are presented in Table 24, along with the approximate experimental values of the equivalent conductance taken from data of A. Woo (8).

The values of B, B_1, and B_2 were evaluated using the value of 78.54 for the dielectric constant of water (55), and a value of 298.15°C for T. The equivalent conductance of NaOH at infinite dilution was taken to be 247.8 ohm^{-1} (56). The value for a^o, the radius of hydration of the ion, was used as a variable parameter. A value between 3.5 - 4.5 Å is generally used in evaluating the conductance parameters for most salts. By varying a^o over a wide range of values, it can be seen from Table 24 that all values of calculated equivalent conductance are below the experimental results. The correction of bulk viscosity of the solutions over corrects the equivalent conductance.

Table 24. Calculated Equivalent Conductances for the Sodium Hydroxide Solutions at 25.0°C using the Wishaw-Stokes Equation

Normality	a° Values 3.0	3.5	4.0	4.5	7.0	9.0	10.0	11.0	14.0	Exp.[a]
2.0681	112.81	115.78	118.26	120.34		129.70	130.50	131.04	131.35	146
4.2106	61.69	63.76	65.42	66.77	70.44	71.16		70.61		96
6.3051	33.91	35.16	36.13	36.88		38.08		36.52		60
8.3794	18.67	19.38	19.91	20.30						38
10.3664	10.93	11.34	11.64	11.84	11.82	10.83		8.90		23
12.2502	6.88	7.14	7.31	7.41						16

[a]Values extrapolated from equivalent conductance graph of A. Woo (8).

DISCUSSION AND CONCLUSIONS

Nature of NaOH and KOH Solutions

It has long been proposed that ions in solution disrupt the ordering of molecules in a solvent. The cause of this disruption in water solution has been looked at from many directions.

G. Akerlof et al. (15, 16), while working with the densities of aqueous solutions of NaOH and KOH, noted that the graph of the apparent partial molal volume versus the square root of the concentration of the NaOH solution had a sharp break at higher concentrations while the graph for the KOH solution slowly changed from a linear relationship to one of a quadratic relationship. For NaOH solutions the break shifted to higher concentrations as the temperature of the solutions increased. At 0.0°C the break occurred at a concentration of 10 molal. Akerlof thought these changes to be due to changes in the packing of the water molecules around the ions. No inferences were made as to how this could be brought about.

N. M. Baron and R. P. Matveeva (19) have looked at the complexity of the log viscosity versus concentration curve for aqueous NaOH solutions. By drawing tangents to this curve at various points of concentration, they were able to plot the derivative of the log viscosity divided by the concentration versus the concentration of the solutions. They observed a maximum in the curve at a mole fraction of 0.09 (similar to 5N). They attributed this to the fact that all water molecules are bound in primary and secondary

coordination spheres. They propose that before this point of complete solvation is reached, the increase of viscosity is brought about by ordering of random water molecules into primary and secondary coordination spheres around the ions, and ionic interaction among the ions. After complete solvation of the ions has occurred, there is a sharp decrease in the viscosity with increased concentration. They predict that now only the ionic interactions are having an influence on the viscosity of the solution.

From the viscosity studies of this work there does not appear to be the complexity in the KOH log viscosity versus concentration curve that there is in the NaOH curve. One can only speculate as to whether complete solvation has occurred or, as in the case of density, if the change is just more gradual.

Jamz et al. (22) take the point of view that the structure of concentrated solutions approaches that of its crystal hydrate such as are formed by solute-solvent pairs. They believe that as the concentration of the solute increases there is a transition of the water structure from that of pure water to that of the crystal hydrate. Several observed properties of these solutions that they believe supported their proposal are the maximum in a specific conductance versus concentration curve, a minimum in a log $\eta\Lambda/\eta_0$ versus log concentration curve, and definite breaks at high concentrations in mobility ratio versus concentration curves.

A. Woo (8) has shown that NaOH and KOH solutions exhibit a maximum in an equivalent conductance versus concentration curve. The NaOH has

a maximum at about 5N and KOH at about 7 N for the solutions at 25.0°C. In looking at the equivalent conductance-viscosity product versus concentration, the KOH solutions showed a minimum at about 8 N for the solutions at 25.0°C. The NaOH solutions did not exhibit a minimum in the range of solutions studied.

W. Good (54) has also looked at the problem. He was especially interested in seeing if the H^+ and OH^- ions might have any unique properties, since they originate from water itself, and have mobilities far exceeding any other ions. From earlier papers Good had concluded that ionic hydration and its effects on bulk water determines the fluidity of aqueous electrolytes.

As the hydroxide concentration of a 1:1 electrolyte increases in an aqueous solution, the structure of the water is broken down. This is accompanied by the decrease in the entropy of activation, ΔS^*, of the fluid flow of the solution. The hydroxide ion according to Good is more heavily hydrated than the hydrogen ion, and it appears to create more disorder. The details of the structure of the hydrated hydroxide ion are not known.

KOH and NaOH differ in their structure breaking effects as is evidenced by the decreasing entropy of activation of fluid flow of the solution. The entropy versus concentration curve for KOH decreases sharply and then levels off at higher concentrations, while the curve for NaOH is less pronounced.

Other differences between NaOH and KOH solutions were also pointed out by Good. NaOH appears to be more complex in its behavior. At

lower temperatures NaOH forms a large number of hydrates in concentrated solution, while KOH exhibits only three in the 40 - 80 % concentration range. Recent transference number studies show the similar behavior for KOH, and the possibility of $Na(OH)_x^{-x+1}$ complexes are suggested. The mobilities of the Na^+ and K^+ ions become about equal as the temperature of the solution increases. Good attributes this to the fact that less complexes can be forming for the NaOH and there is much more disorder in the orientation of the water molecules due to thermal motion of the ions and water molecules.

Robinson and Stokes (57) point out another theory on the effect of ions on water. The field intensity of the ion greatly affects the neighboring water molecules and disrupts them from their normal order. In dilute solutions one can imagine successive layers of water molecules surrounding an ion. As the concentration increases, the number of water molecules available for ionic bonding to each ion decreases until there is only one layer allowable. Needless to say the water in the fixed layer around the ion must be firmly bound. Even if the water bound in this first layer were bound in similar orientation, to that of the native water, the effects that this would have on the outer layer would be to cause disorder in the normal water structure.

Until recently it was not even known if the dielectric constant of water would be raised or lowered by the addition of an electrolyte. Work done by Hasted, Ritson, and Collie (58) has shown that the bulk dielectric constant decreases with the addition of an electrolyte. This drop in dielectric constant appears to be linear up to

concentrations of 2 N. After that the decrease is less than that predicted by linearity, at least for the solutions for which measurements were made possible.

Thus this decrease in the dielectric constant would make it possible for the ions to arrange the water molecules around themselves easier, and indeed the solution structure would be approaching that of the crystal hydrate.

Comments on Theories Used

One of the ideas to result from the zero mobility concept proposed by C. A. Angell (36, 41) and C. T. Moynihan (39) is the fact that the constant T_o should be constant for a particular solution no matter which transport process it was derived from, be it equivalent conductance data, viscosity data, or diffusion coefficient data. All transport processes are considered to be similar. For the T_o values derived from viscosity and equivalent conductance data, there does not appear to be good agreement at all. From Tables 21 and 22 where T_o is derived from the viscosity and equivalent conductance data, these comparisons can be made:

Viscosity Data		Equiv. Conductance Data	
normality	T_o	normality	T_o
2.068	130.8	2.332	25.0
8.379	164.4	8.358	143.4
12.250	180.9	12.04	143.8

Although the experimental error could be large, the errors here are far greater than what could be expected of experimental errors alone. Thus an error in the theory must be assumed.

Another consequence of the zero-mobility concept proposed by C. A. Angell (36, 41) and C. T. Moynihan (39) is the expression for equivalent conductance and fluidity $\Lambda, 1/\eta = A\exp\left[-k/(N_o - N)\right]$ where N_o is the zero mobility concentration (equivalents/liter) at which zero mobility occurs when T_o and T (the glass temperature) are the same.

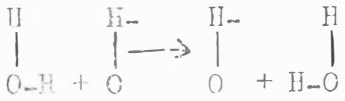
G. J. Janz et al. (22) have found that N_o for the equivalent conductance and fluidity do not coincide. For the solutions they studied, the following results were: $NaNO_3$ $N_o^{\Lambda} = 46$, $N_o^{\phi} = 29$; $NaClO_4$ $N_o^{\Lambda} = 32$, $N_o^{\phi} = 19$, NaCNS $N_o^{\Lambda} = 23$, $N_o^{\phi} = 20$.

This inconsistency also places a strain on the zero mobility theory. There is some merit in the fact that the temperature dependence of all these transport processes can be described in a similar manner, but the opinion of this author and of several others who have tried the theory is that more work is needed to find a more adequate function to describe the process.

The failure of the Wishaw-Stokes equation should also be looked at. Obviously, some assumptions or simplifications made were not valid. Since all of the calculated equivalent conductance are high without the viscosity correction, this indicates that the viscosity correction is needed. But the fact remains that the correction as it stands over corrects the situation. The equation could be modified

to include a different viscosity function, but there may be other factors that are not being considered.

When working with acids and bases the mobility of the hydrogen and hydroxide ions is very large compared to the other type of ions present. Various mechanisms have been proposed to attempt to explain this process (57). Since this work is with bases, the mechanism proposed for bases is a chain mechanism involving the hydroxide ion. Since it originated from water itself, it may be possible for the hydroxide ion of the base to exchange with an hydroxide group of a water molecule in the following manner:



This could account for the high experimental equivalent conductances of the NaOH and KOH solutions, because no allowance for this type of interaction has been accounted for in present theories.

The dielectric constant of the solutions is another factor that needs to be considered in any theory. In very dilute solution, the dielectric constant is lowered, but not to any great degree. Hasted, Ritson, and Collie (58) have measured the lowering of the dielectric constants of several acids, bases, and salts up to concentrations of a few tenths molar to five molar. They found the lowering to be linear up to 2 N in some cases, but the decrease in the dielectric constant diminishes somewhat after that. J. H. Christensen, et al. (59) have found that with concentrated phosphoric acid solutions, the dielectric constant actually goes through a minimum. The minimum

dielectric constant reached was 19.2 at a concentration of approximately 75% phosphoric acid. For a 5.6 NaCl solution at 25.0°C the dielectric constant had already dropped to 32.1. When the dielectric constant of pure water at 25.0°C is considered to be 78.54, this is a very significant change that should be accounted for. Due to the high conductivity of the solutions, it is difficult to measure the dielectric constant of the NaOH and KOH solutions and may other electrolytic solutions accurately. This has been one of the limiting factors that is holding back progress in this area.

The lowering of the dielectric constant makes it easier for the ions to exert an electrostatic force on the water molecules. As a result the water becomes more tightly bound to the individual ions. Janz's theory that the water structure of the concentrated solution changes from that of pure water to that of the crystal hydrate may be supported by this fact.

A treatment of the influence of the dielectric constant on the conductivity of the electrolytic solution will have to be made. Previous expressions for the electrostatic field forces of the ion may have to be modified to include the changes in the dielectric constant and the chain mechanisms of the mobility of the hydroxide and hydrogen ions.

There has been one other assumption made that should be reviewed. It has been assumed that the degree of hydration of an ion is constant over all concentrations, or at least that the radius of the hydration

sphere is constant. From the data in Table 24, it can be seen that there is a maximum in the equivalent conductance values calculated for each solution. As the concentration of the solution is increased, the maximum value of the equivalent conductance occurred at lower and lower a^{o} values. The limiting a^{o} value may be the crystalographic a^{o} value for a particular hydrate of NaOH. It would be interesting to compare the a^{o} values of various hydrates of NaOH with the a^{o} values of different concentrations of the solutions. However, the stability of some of these hydrates may make the measurements difficult.

As the concentration of the solutions increases, there are fewer water molecules available for the ions to interact with. For example, a 0.20 mole fraction solution of NaOH contains 20 moles of NaOH for 80 moles of water. The NaOH is in ionic form; therefore, there are 20 moles of Na^{+} ions and 20 moles of OH^{-} ions. There is a total of 40 moles of ions in the solution. The number of water molecules that could be associated with each ion can not be over two. Therefore, hydration numbers of ten that have been reported for some ions are meaningless in highly concentrated solutions.

From the conclusions reached in this research, it is obvious that theories used to explain transport properties, such as electrical conductance, for dilute solutions can not be used in their present or modified forms. New approaches must be taken, for the problem is very complex. Another question that many researchers ask is, "Does the bulk viscosity and dielectric constant give an accurate picture

of the microscopic properties experienced by the ions?" If there is no relationship between the two, what measurements could be made? A better understanding of molten crystal hydrates may help to provide an answer to the problem of the behavior of highly concentrated solutions.

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